

Chemical contaminant risks associated with in-water cleaning of vessels

John A Lewis

ES Link Services Pty Ltd, Castlemaine, Vic



© Commonwealth of Australia 2020

Ownership of intellectual property rights

Unless otherwise noted, copyright (and any other intellectual property rights) in this publication is owned by the Commonwealth of Australia (referred to as the Commonwealth).

Creative Commons licence

All material in this publication is licensed under a Creative Commons Attribution 4.0 International Licence except content supplied by third parties, logos and the Commonwealth Coat of Arms.

Inquiries about the licence and any use of this document should be emailed to copyright@awe.gov.au.



Cataloguing data

This publication (and any material sourced from it) should be attributed as: Lewis, JA 2020, *Chemical contaminant risks associated with in-water cleaning of vessels*, Department of Agriculture, Water and the Environment, Canberra, September. CC BY 4.0.

ISBN 978-1-76003-321-7

This publication is available at awe.gov.au/publications.

Department of Agriculture, Water and the Environment GPO Box 858 Canberra ACT 2601 Telephone 1800 900 090 Web awe.gov.au

The Australian Government acting through the Department of Agriculture, Water and the Environment has exercised due care and skill in preparing and compiling the information and data in this publication. Notwithstanding, the Department of Agriculture, Water and the Environment, its employees and advisers disclaim all liability, including liability for negligence and for any loss, damage, injury, expense or cost incurred by any person as a result of accessing, using or relying on any of the information or data in this publication to the maximum extent permitted by law.

Acknowledgements

The author thanks Bianca Brooks, Timothy Carew, Peter Wilkinson and Sonia Gorgula (Department of Agriculture, Water and the Environment) Rupert Summerson (ABARES) and Eugene Georgiades (Biosecurity New Zealand, Ministry for Primary Industries) for their feedback and input in preparing this report.

Foreword

Biofouling is a major pathway for marine pest entry into Australia. The Australian Government committed to the management of biosecurity risks associated with biofouling through implementation of the *Biosecurity Act 2015* (Biosecurity Act). The Department of Agriculture, Water and the Environment has statutory powers under the Biosecurity Act to respond when a vessel's biofouling presents an unacceptable biosecurity risk of introducing and spreading marine pests and associated diseases.

To manage this risk, the department has proposed mandatory biofouling management requirements for vessels arriving in Australian Territory. Under these requirements vessels would manage biofouling to a best-practice standard, effectively and efficiently reducing biofouling and the risk it poses to our environment and economy.

In-water cleaning involves removing the biofilm and fouling from the hull of a ship using mechanical methods, such as brushes or water jets. This can either be done proactively, as part of a biofouling management plan, or reactively, to remove biofouling on vessels in which preventative management has been ineffective or inadequately maintained. A number of factors influence the potential for environmental harm associated with contaminant release due to inwater cleaning. These include the type of paint, the type and coverage of fouling, the type of cleaning method used, the physical parameters of the vessel location, and the frequency of cleaning within a location.

The department is progressing new standards for in-water cleaning to mitigate the potential for environmental harm relating to biosecurity and contaminant risks in association with in-water cleaning of vessels' biofouling. A standard will provide assurance to ports, vessel owners and other stakeholders that contaminant and biosecurity risks are effectively and appropriately managed. It will also provide clear performance targets for in-water cleaning technologies and support technological innovation for the development of more efficient in-water cleaning systems.

This report compiles available information on the chemical contaminant risk posed by the grooming and in-water cleaning of biofouling on vessels with biocidal antifoulant coatings taking into account a variety of factors that influence this risk.

This report is part of a number of information inputs that will inform the development of new national standards for in-water cleaning in Australia.

Marine Biosecurity Unit Animal Biosecurity Branch Department of Agriculture, Water and the Environment

Contents

Forewordiii					
Summaryvi					
Introduction1					
1	Antifouling coatings				
	1.1	Biocidal coatings	2		
	1.2	Biocide-free coatings	4		
	1.3	Antifouling coating system efficacy	4		
	1.4	Antifouling biocides	5		
	1.5	Non-active coating constituents	11		
	1.6	Uncoated metallic surfaces	12		
	1.7	IWC Recommendations	12		
2	Contaminant sources 1				
	2.1	Coatings	13		
	2.2	Unpainted metals	15		
3	Source contamination				
	3.1	Biofilms	16		
	3.2	Primary and secondary fouling	16		
	3.3	Leached layer	17		
	3.4	Sound paint	17		
	3.5	Paint flakes	17		
	3.6	IWC Recommendations	18		
4	Cleaning scenarios		20		
	4.1	Grooming & cleaning	20		
	4.2	Cleaning contaminant levels	23		
	4.3	In-water Cleaning Recommendations	24		
5	Cleaning & capture requirements				
	5.1	Effluent standards	26		
	5.2	Passive leaching	26		
	5.3	Discharge modelling	28		
	5.4	Contaminant release from in-water cleaning	29		
6	Coating suitability & acceptability for in-water cleaning				
	6.1	Coating	33		
	6.2	Biofouling	35		
7	Recor	nmendations on in-water cleaning with respect to contamination	38		

7.1	What to clean	38		
7.2	When to clean	38		
7.3	When not to clean	38		
7.4	How to prepare for IWC	39		
7.5	Risk assessment of the IWC	39		
7.6	How to clean	40		
7.7	When to contain the waste	40		
7.8	When to treat the waste	41		
7.9	In summary	41		
Appendix A: Australian Pesticides and Veterinary Medicines Authority approved antifouling products				
Appendix B: Risk assessment of chemical discharge from in-water cleaning				
Glossary				
References				

Tables

Table 1 RAC and PNEC for antifouling biocides	28
Table 2 Copper content of different surfaces removed during in-water cleaning	29
Table 3 Layer thickness and removal depth during in-water cleaning	29
Table 4 Copper release rates for recreational and commercial vessels	30
Table 5 Level of Fouling (LOF)	36
Table 6 Fouling Ratings Scale	36
Table A1 APVMA Approved Antifouling Products, 2020-03	44

Summary

The Department of Agriculture, Water and the Environment is developing new national standards for in-water cleaning (IWC) of biofouling in the Australian Territorial Sea. This was a direct recommendation of a 2018 review of the uptake and effectiveness of the 2015 Australian and New Zealand Anti-Fouling and In-Water Cleaning Guidelines (the Guidelines) that was undertaken by the Marine Pest Sectoral Committee.

While the Guidelines provide a framework for decision-makers to assess the potential for inwater cleaning activities to cause harm through the release of antifouling biocides and nonindigenous marine species; the uptake of the Guidelines in Australia has been low. In part, this is a result of an unclear approval process for developers and users of IWC technologies, which has highlighted the need to clarify decision-making processes, roles, and legislative frameworks. With an increase in IWC requests and increase in regulation of risk associated with biofouling in the Australasian region, it is timely to develop a new standard for IWC that can facilitate environmentally responsible cleaning activities.

This report assesses the current knowledge on the potential for risks associated with the chemical contamination of the environment from IWC of vessels and, where necessary, provides recommendations on contamination mitigation and/or treatment measures. Biosecurity risks associated with in-water cleaning are not within the scope of this report, however, are being addressed in two separate parallel studies. One study assessed the minimum viable propagule sizes of macrofouling organisms that could be released during IWC and another modelled IWC cleaning scenarios in three different Australian port environments.

The primary method to limit the growth of marine organisms on vessel hulls is the application of coatings that prevent or deter the settlement, attachment and/or maturation of organisms on immersed surfaces. This is typically achieved by one of two mechanisms:

- "antifouling" biocides contained within the coating that are released at or through the coating surface (biocidal coatings)
- coating surface properties that deter settlement or facilitate the dislodgement of attached organisms (biocide-free coatings).

An effective biocidal coating functions by the continual release of biocide at the coating surface at a rate sufficient to prevent the attachment of biofouling species. These coatings, which are mostly applied as paints, release the biocide, or biocides, into the seawater by one of several chemical mechanisms that enable biocide dissolution at the coating surface.

Very few biocides have the characteristics needed for use as an effective antifoulant while being environmentally benign. In Australia antifouling biocides and products need approval from the Australian Pesticides and Veterinary Medicines Authority (APVMA) for import, manufacture, sale and use, and there are only eight biocides used in the 52 currently approved products. Copper, in the form of cuprous oxide or cuprous thiocyanate, is the primary biocide used in antifouling coatings (AFCs), as it has been for more than a century, and is present in 50 of the AFCs approved by the APVMA. Approval of some other biocides has not been granted or has been revoked by the APVMA. Many more AFCs are available for application to vessels overseas and, with the exception of coatings prohibited under the International Maritime Organization's International Convention on the Control of Harmful Anti-fouling on Ships (IMO AFS Convention), there are no restrictions on these vessels entering Australian waters. Antifouling coatings on international vessels may include older biocides that are no longer approved by the APVMA, new biocides that are yet to be submitted to the APVMA for approval or, commonly, biocides which have been approved by APVMA, but where approval of the formulated product has not been sought because approval costs cannot be justified due to the small market and lack of facilities for painting of large ships in Australia.

The process of biofouling development starts with the adsorption of a film of organic and inorganic matter from the seawater, followed by microbial colonisation of this film by bacteria, microalgae and protozoans. This occurs on all surfaces, whether non-biocidal or biocidal. On biocidal coatings, bacteria and microalgae often exude polysaccharides or other substances (slime) that ameliorate the toxicity of the biocide to the microbes. On non-biocidal surfaces, several days to weeks after first immersion, multicellular organisms will settle, attach and grow. An effective antifouling coating will maintain the biofouling development at the biofilm stage until the biocide release rate drops below that necessary to prevent macrofouling attachment.

On biocide-free coatings or surfaces, macrofouling development is largely unconstrained but, for fouling release coatings, the strength of adhesion is reduced, and organisms can be dislodged by turbulent water movement across the surface, or light mechanical force.

Once a biocidal surface is immersed, biocide release will commence through the process of hydrolysis, hydration and/or dissolution at the coating surface. This changes the surface composition of the coating and three different layers develop: the innermost sound layer of unreacted paint, the leached layer from which biocide has dissolved but the skeletal paint matrix remains, and the surface biofilm of microbes and their extracellular exudates.

Three types of IWC can be defined: hull grooming, proactive cleaning, and reactive cleaning.

Hull grooming is regular cleaning to remove the biofilm, surface deposits, and friable surface from hull surfaces to reduce surface microroughness and viscous drag. The benefit of hull grooming is improvement in ship performance and efficiency which reduces environmental impact by reducing drag, fuel consumption, greenhouse gas emissions and costs. Grooming can also eliminate the need for high intensity hull cleaning methods and increase coating longevity. Hull grooming is generally restricted to the planar surfaces of the hull that are prone to hydrodynamic drag. Propeller polishing can be considered similar to hull grooming, as it is undertaken to restore the propulsion efficiency of propellers.

Proactive IWC is the removal of early stages of biofouling to prevent the growth and maturation of macrofouling organisms on both hull surfaces and on and within hull niches, which, if established, can significantly impact on vessel efficiency and facilitate marine species translocation. Reactive IWC is the removal of established macrofouling to restore hull efficiency or remove growth considered to pose a biosecurity risk.

Hull grooming and proactive IWC are similar in removing the surface biofilm and, if present, the early, microscopic stages of newly settled macrofouling, and some or all of the leached layer. Reactive IWC removes hard and soft macrofouling, together with underlying and spatially interspersed biofilm, and friable leached layer. If aggressive cleaning methods are used for

proactive or reactive IWC, the outer surface of sound paint underlying the leached layer may be removed. Paint flakes may also be removed during IWC if the paint system is damaged or defective. Biocide concentrations are higher in sound paint and paint flakes than in the leached layer and/or biofilm.

The Guidelines recommend that, for contaminant discharges, the "contaminant discharges must meet any local standards or requirements". However, Australian Government, State or Agency regulatory standards that are directly relevant to discharges from IWC systems are not identified. Satisfying authorities that contaminant discharges from IWC are acceptable has therefore proven difficult. MAMPEC (Marine Antifouling Model to Predict Environmental Concentrations) is an integrated hydrodynamic and chemical fate model, developed to predict environmental concentrations for the exposure assessment of antifouling substances. The model has been validated for a number of compounds and has been recognised by regulatory authorities in the EU, other OECD countries, the USA, Japan, New Zealand and Australia. MAMPEC-BW was developed for the IMO to enable exposure assessment of chemicals used in ballast water management systems. Limited testing of the utility of MAMPEC-BW for assessing contamination from IWC treatment systems has been undertaken and it is suggested as a suitable approach to model environmental risks associated with IWC. The model calculates the predicted environmental concentration (PEC) of biocides, which can then be compared to environmental protection standards.

IWC may occur

- without capture or containment of removed biological and chemical waste
- with capture, containment and mesh filtration of the waste stream
- with capture, containment, mesh filtration and treatment of the waste stream.

To contain potential risk associated with chemical contaminants, capture, containment and mesh filtration would remove paint flakes and biocide contamination associated with the biological waste, but not dissolved or particle-associated chemical contaminants. Adding treatment of the filtrate, by cartridge filtration after mesh filtration, has been demonstrated to significantly reduce the dissolved (and overall) copper concentration in the waste stream.

To ensure in-water grooming and cleaning does not result in potentially harmful chemical concentrations in local waters, IWC should:

- be restricted to areas where growth on wetted surfaces is considered unacceptable to vessel operators or for biosecurity compliance, and the least aggressive and most appropriate methods used to achieve the required result. The cleaning method should be chosen to ensure the coating is not damaged. A combination of methods is likely to be required for the outcome of a 'clean hull'
- capture and contain paint waste if the coating system is defective and paint flakes are likely to be removed during cleaning
- be monitored to ensure the cleaning method is not damaging the coating system
- if the IWC is to be conducted in a semi-enclosed, inshore environment and/or in close proximity to sensitive areas/threatened species per the Environment Protection and Biodiversity Conservation Act 1999 (EPBC Act) and all, or sections of the hull plate on the

vertical sides and/or flat bottom are to be groomed or cleaned, be subject to pre-emptive risk assessment to determine

- firstly, acceptability of hull grooming without waste capture and treatment for vessels up to a specified size in specified locations
- secondly, acceptability of capture, containment and treatment systems to ensure the low risk of discharges from IWC or hull grooming not acceptable under the previous point.

IWC should <u>not</u>:

- damage the coating
- cut deeply in to sound paint below the leached layer
- be performed in shallow, semi-enclosed water bodies without an acceptable risk assessment
- be permitted if the vessel does not have a valid International Anti-Fouling System Certificate or Declaration on Anti-Fouling System that lists biocides present in the coating
- be permitted if the AFC contains diuron, cybutryne, ziram, chlorothalonil, or other biocides restricted or banned elsewhere in the world
- be permitted if the specified service-life for the antifouling systems applied at the last drydocking has been exceeded
- be permitted if the end of the service life and scheduled dry-docking is within 3 months for hull grooming and proactive cleaning or 6 months for reactive cleaning
- be undertaken if there is extensive significant coating system breakdown with flaking or lifting of the paint. The vessel should, instead, be dry-docked for coating system repair, renewal or replacement
- be undertaken without capture and, for biocidal coatings, treatment if there are areas of significant breakdown and cleaning is required for emergency reasons such as marine pest emergencies.

To refine and improve outcomes of the above recommendations on risk assessment, additional data of benefit could include:

- if not already available, physical and hydrological parameters for harbours and other water bodies where IWC could be undertaken to define those locations in MAMPEC modelling
- additional measurements of the biocide content of the leached layer and surface biofilms, including different AFC types and ages.

Introduction

The accumulation of organisms on the wetted surfaces of vessels, commonly known as biofouling, is a major issue for shipping worldwide, causing reductions in vessel performance and fuel efficiency, and increasing vessel emissions. Vessel biofouling is also a vector for the translocation and establishment of marine pests, which can have serious impacts on marine environments and industries.

In-water cleaning can increase vessel efficiency and manage biosecurity risks by removing the biofilm and fouling from the hull of a ship using mechanical methods, such as brushes or water jets. This can either be done proactively, as part of a biofouling management plan, or reactively, to remove biofouling on vessels in which preventative management has been ineffective or inadequately maintained. Whilst in water cleaning or treatment is an important tool for managing biofouling it also presents a number of biosecurity and water quality risks which need to be managed to ensure that cleaning is not deleterious to the environment.

The Department of Agriculture, Water and the Environment (department) is developing national standards for in-water cleaning (IWC) of biofouling in the Australian Territorial Sea to manage the biosecurity and contaminant risks posed by IWC. This was a direct recommendation of a 2018 review of the uptake and effectiveness of the Australian and New Zealand Anti-Fouling and In-Water Cleaning Guidelines (the Guidelines) that was undertaken by the Marine Pest Sectoral Committee.

Development of a national IWC Standard will provide vessel owners and operators and in-water cleaning companies with a tool to manage the environmental risks posed by vessel biofouling and by in-water cleaning operations within the Australian Territorial Sea, particularly in light of proposed mandatory Australian Biofouling Management Regulations. The standard would outline the requirements for undertaking in-water cleaning and the standards for discharge and capture of biological matter. Chemical release from IWC will be required to meet the legislative requirements of the local region where the cleaning is to occur.

The department is gathering scientific, technical and applied expertise to fill knowledge gaps surrounding risks associated with in-water cleaning of biofouling. This information will contribute to the development of the evidence base that supports the development of a new national standards for in-water cleaning (IWC) and support decision-making in relation to the treatment of effluent from IWC.

This report addresses the potential for contaminant risks to be present in association with inwater cleaning of vessels and where necessary, recommended management measures. The report also discusses the appropriateness of different methods of IWC, with consideration given to antifouling coating (AFC) type, age, and condition; the factors that influence efficacy of AFCs (e.g. applicator, conditions of application etc.), and makes recommendations on how to take this variability into account.

1 Antifouling coatings

All surfaces immersed in the sea become potential sites for colonisation by marine species which can attach directly to the surface, or on, within or between species that have already established on the surface. When the attachment or establishment of these species or communities is unwanted or deleterious, it is commonly termed fouling or biofouling (Dürr 2010). Efforts to prevent or limit fouling growth on vessel hulls date back to at least the Phoenicians who, at around 400 BCE, applied a mixture of arsenic, sulfur and oil to the sides of their vessels (Callow 1996). The following overview on the prevention of biofouling on underwater surfaces draws on, and augments, information in a series of previously published papers and reports (Lewis 1998, Lewis 2002, Lewis 2010, Dafforn et al. 2011, Morrisey et al. 2013, Lewis 2018).

The primary method to limit the growth of marine organisms on immersed vessel surfaces is the application of coatings that prevent or deter their settlement, attachment and/or maturation. This is typically achieved by either the coating containing "antifouling" biocides that are released at or through the coating surface (biocidal coatings), or by having surface properties that deter settlement, or facilitate the dislodgement of attached organisms (biocide-free coatings).

1.1 Biocidal coatings

An effective biocidal coating functions by the continual release of biocide at the coating surface at a rate sufficient to prevent the attachment of biofouling species. When this rate drops below the critical value, species will begin to settle, with the initial colonisers those species with the highest tolerance to the biocide.

These coatings, which are mostly applied as paints, release the biocide, or biocides, into the seawater by one of several chemical mechanisms that enable biocide dissolution at the coating surface.

1.1.1 Soluble matrix (ablative)

The biocide, or biocides, are dispersed through a sparingly soluble paint matrix. Hydration causes the surface to slowly dissolve to enable the dissolution on the freely associated biocide. Conventional soluble matrix coatings utilise natural rosin as the matrix. The dissolution rate in newer ablative coatings, sometimes called controlled depletion polymer (CDP) coatings, has been improved by combining polymeric ingredients with the seawater soluble binder, but the mechanism remains a hydration/dissolution process.

The service life of soluble matrix coating can be between 18 and 36 months, varying with formulation and service conditions. Inconsistent ablation and a relatively thick biocide-depleted surface ("leached layer") can reduce biocide release rates and lead to premature failure, as can the formation of insoluble precipitates on the coating surface.

1.1.2 Insoluble matrix (contact leaching/diffusion/hard)

As the name suggests, the binder in these coatings is insoluble and biocide release depends on the biocide particles in the dry paint to be of a density that enables direct contact between them. As biocide particles close to the surface dissolve, microchannels form within the coating that enable biocide particles deeper in the film to dissolve and move out of the coating through the microchannels. Insoluble matrix coatings were harder and physically more durable than conventional soluble matrix coatings but, with time, the skeletal matrix becomes clogged with insoluble degradation products, resulting in a drop in biocide release rates to below effective levels.

Effective service life is generally less than 24 months. Thick leaching layers and insoluble surface precipitates can cause premature failure.

1.1.3 Self-polishing copolymer (SPC)

Unlike soluble matrix coatings, the mechanism of biocide release from SPC coatings is through hydrolysis of the copolymer paint matrix. When exposed to seawater, the copolymer cleaves, and part is released. The residual backbone of the copolymer is soluble and is then released. The first SPC antifouling coatings were the tributyltin (TBT) methacrylate copolymers, in which hydrolysis released the biocidal TBT moiety, followed by dissolution of the methacrylate backbone. Co-biocides were added to some TBT SPC coatings to boost performance, particularly for slow or low activity vessels.

Superior performance to conventional coatings was achieved due to the controlled nature of the process providing consistent biocide release rates throughout coating service life, polishing of surface micro-roughness to smooth the coating in service, and minimal development of leached layers.

Replicating the self-polishing mechanism in tin-free coatings was challenging to the paint industry, but effective copper, zinc and silyl acrylate coatings are now available which provide similar service lives to the TBT SPCs. In contrast to TBT SPCs, the biocide is not part of the copolymer, rather the biocides are mixed through the paint.

SPC coatings can provide a service life of up to 90 months, depending on the formulation, vessel operational profile, and application thickness. Specific formulations are marketed for high speed and/or high activity vessels ("hard" formulations), low speed and/or low activity vessels ("soft" formulations), and for low activity and/or static vessel and installations. Premature failure can occur if, for example, a hard formulation is on a vessel that has little activity and the polishing rate induced by water flow is insufficient to erode the coating at the rate required to generate the critical biocide release rate. Surface deposits under low flow conditions can also obstruct effective polishing.

In some formulations, termed hybrid CDP/SPC coatings, rosin is added to reduce the cost of the product when the service interval achievable with pure SPC coatings is not needed.

1.1.4 Biocidal fouling release

Biocide-free silicone fouling release coatings discussed in more detail in Section 1.2 can foul under static or low activity conditions. A silicone-based foul release coating is available that contains a biocide to boost static performance.

1.1.5 Metallic

Sheathing of wooden ships with copper sheeting was the first authenticated antifouling treatment and dates back to the mid-1700s. The antifouling mechanism is the release of copper ions as the metal corrodes. The widespread use of copper sheathing was superseded by antifouling paints in the late 1800s, driven by the introduction of iron ships which could not be sheathed with copper because of the induced galvanic corrosion. Sheathing of wooden and

fibreglass hulls with cupro-nickel sheet does still occur but is uncommon. The more common antifouling application of cupro-nickel alloys is for seawater pipework.

A variant of metal sheathing is the incorporation of cupro-nickel particles or flakes into, or onto, an epoxy or other polymer matrix. These coatings are hard and impervious, with the antifouling effect dependent on metal particles being exposed to seawater at the surface. The coatings are not considered practical for vessels but are used on offshore and fixed installations and can be effective for 60 months or more.

1.2 Biocide-free coatings

Biocide-free coatings for biofouling management are mostly either coatings that minimise the adhesion strength of biofouling organisms, called foul or fouling release coatings (FRC), or hard, durable (mechanically resistant) coatings that have no active antifouling property, but are able to be regularly scrubbed to remove established marine growth.

1.2.1 Fouling release

Most FRCs are formulated using silicone elastomers or fluoropolymers to create a surface to which macrofouling organisms cannot securely adhere. Some species are able to attach and grow under static conditions but can be easily dislodged by turbulent water flow across the surface, or by non-aggressive physical cleaning methods.

FRCs can be effective for 60 months or more, with the main cause of failure a consequence of mechanical damage due to the susceptibility of these elastomeric coatings to abrasion damage. FRCs can have better durability than biocidal coatings on sharp edges and projections, for example on sea chest intake grate bars, because of the better edge retention of elastomeric coatings.

1.2.2 Mechanically resistant

These coatings are hard, smooth, and abrasion resistant and are able to withstand mechanical cleaning, ice scour and other abrasive forces. They can be epoxy, ceramic/epoxy, or epoxy/glass flake formulations.

Mechanically resistant coatings are extremely durable and would not require renewal for 90 months or more. However, with no inherent mechanism to prevent biofouling attachment and growth, regular cleaning is required to keep the surfaces clean exposed to a biofouling environment.

1.2.3 Other biocide-free coatings

Fluorinated polymer coatings, smart polymers, hydrophilic surfaces, fibre coatings and nonleaching coatings have all been proposed as non-toxic alternatives for antifouling prevention, but none of these technologies have yet demonstrated the performance or cost-effectiveness needed for adoption (Lewis 2009).

1.3 Antifouling coating system efficacy

An effective antifouling coating system is one that is free of secondary biofouling, such as acorn and gooseneck barnacles, bryozoans, hydroids, serpulid worms, spirorbid worms, algal tufts, coralline algae and/or amphipods. For a biocidal coating, this is achieved by the continuous release of a biocide, or biocides, at the surface of the coating at a rate that prevents attachment of macrofouling organisms. If the rate of biocide release drops below the minimum concentration needed to prevent settlement, macrofouling organisms will begin to attach, the first organisms will be those with the highest tolerance of the biocide or biocides. On a copperbased AFC, the first macrofouling organisms to settle are commonly encrusting bryozoans (*Watersipora* spp.), then serpulid tubeworms (*Hydroides* spp.), acorn barnacles (*Amphibalanus* spp.), erect bryozoans (*Bugula* spp.) and, in areas with high exposure to sunlight, green algae (*Ulva* spp.) (Wisely 1958, Callow 1990, Blossom et al. 2016).

Some of the reasons for a premature failure of different biocidal coating types are discussed in <u>Section 1.1.1</u>. However, early failure of an AFC can sometimes result from adverse conditions at the time of paint application, inadequate surface preparation, or incompatibility of coatings (Fitzsimons 2011). Technical (or Product) Data Sheets or instructions on the paint can label, specify the requirements for good application results, including surface preparation, acceptable environmental conditions, application method and recommended coating thicknesses, coating compatibilities, drying and curing time, minimum or maximum times before immersion, etc. System failures, including but not limited to, paint delamination, blistering, cracking, and sagging, can occur if these requirements are not met (Batra 2014). The coating surface can also become hardened under some environmental conditions, which prevents the initiation of biocide release when first immersed.

Underwater hull coating system application is best performed by professional paint applicators, and the surface preparation and application overseen and approved by an inspector from the paint company (Batra 2014). This is the normal procedure for medium to large vessels in commercial dry-docks or shipyards, but not always the case for smaller vessels painted on slipways or in boatyards (TCS 2004).

A project for the Australian Government in 2004 addressed and made recommendations on antifouling performance standards for the maritime industry (TCS 2004), which included the following passage:

"In appraising current industry practices there was a strong view, particularly among the manufacturers and suppliers of antifouling paints, that deficiencies in the application of these paints was the principal reason antifouling paints failed to achieve their potential service life. Upgrading industry standards by the defining good industry practice and auditing applicators against those standards was seen as important."

1.4 Antifouling biocides

Very few biocides have the characteristics needed for use as effective antifouling biocides. An effective antifouling biocide needs:

- to be sufficiently chemically stable to enable persistence in the paint, but not persistent, bioavailable or bio-accumulative in the environment, thus avoiding consequent harm in the short and/or long term
- to be toxic to the broad spectrum of potential biofouling species at release, but not toxic to applicators or non-target species when released

• to have the chemical properties to dissolve out of the coating at a sufficient, but not excessive, rate over a long period of time.

1.4.1 APVMA approved antifouling biocides

In Australia, where both antifouling biocides and products need approval from the APVMA for import, manufacture, sale and use, there are only eight biocides used in the 52 currently approved products (Appendix A); cuprous oxide, cuprous thiocyanate, copper pyrithione, dichloro-octyl-isothiazolin (DCOIT), diuron, thiram, zinc pyrithione, and zineb. That latter six are primarily used as "booster" or secondary biocides in copper-based antifouling coatings to prevent colonisation by copper-tolerant algae. Diuron, thiram and zineb were "grandfathered" into the national registration scheme, when it was established in the early 1990s, without requiring full assessment (Lewis 2010). DCOIT, zinc pyrithione and copper pyrithione were approved later, and passed full assessment (Lewis 2010). An application was submitted for the approval of cybutryne (also known as Irgarol 1051) in the 1990s, which was, and continues to be used overseas. The application was rejected on the basis of emerging evidence of environmental persistence and impact on seagrass (Scarlett et al. 1999a, 1999b).

Coatings that contain no active constituent, which includes fouling release and mechanically resistant coatings, do not require APVMA approval (APVMA 2020a).

1) Cuprous oxide

Cuprous oxide (dicopper oxide) has been used as a primary antifouling biocide for more than a century. It remains in use after the introduction of alternatives such as mercury, arsenic and organotin compounds, and their subsequent banning due to unacceptable human health or environmental risks (Lewis 2018). The antifouling effect of the copper is achieved through dissolution and release of free cuprous ions (Cu⁺), which provide the toxic effect. The cuprous ion is unstable, and, after release, this rapidly oxidises to form the more stable cupric form (Cu²⁺) (Brooks & Waldock 2009a, 2009b). Cu²⁺ complexes with organic and inorganic ligands within a few micrometres of the hull surface, which significantly reduces copper toxicity (Brooks & Waldock 2009a, 2009b).

Cuprous oxide is the primary biocide in 41of the 52 antifouling products currently approved by the APVMA (<u>Appendix A</u>).

2) Cuprous thiocyanate

The use of cuprous oxide, rather than cuprous thiocyanate, is generally preferred due to its lower cost, better solubility, higher toxicity, and the longer effective life of coatings containing cuprous oxide (Brooks & Waldock 2009b). However, galvanic corrosion of aluminium substrates can be initiated if paints containing cuprous oxide are applied without a completely effective and durable barrier coating between the substrate and the antifouling (Chasse et al. 2020). Mechanical damage, such as scratching to the barrier coating, can cause corrosion of the aluminium. Cuprous thiocyanate has a much lesser corrosive effect and is consequently used as the primary biocide in antifouling coatings for use on aluminium hulls and equipment, such as stern drives (Finnie & Williams 2010). In contrast to the red cuprous oxide, cuprous thiocyanate is colourless and is used when lighter coloured hull coatings are desired (Finnie & Williams 2010).

Cuprous thiocyanate is the primary biocide in 9 of the 52 antifouling products currently approved by the APVMA (<u>Appendix A</u>).

3) Diuron

The primary use of diuron is as a herbicide and algaecide for general weed control on no-crop areas, as a pre-emptive herbicide on pineapple, sugarcane and woody crops, and for weed control in and around water bodies (APVMA 2015a). Approval of diuron as an antifouling biocide has been revoked in the UK (Konstantinou & Albanis 2004). Approval has also been revoked in New Zealand, effective from June 2017 (EPA 2020). A chemical review of diuron by the APVMA, completed in 2012, permitted its continued use for some agricultural applications, but revoked its use for numerous other agricultural, non-agricultural and industrial applications because of potential harm to aquatic environments (APVMA 2015a). Continued use in antifouling paints was approved because the contribution to the environmental load from this source was considered relatively small compared to agricultural use (APVMA 2015a).

Diuron is a secondary biocide in 8 of the 52 antifouling products currently approved by the APVMA (<u>Appendix A</u>).

4) Thiram

The primary use of thiram is as an agricultural fungicide, with approval for its use as an antifouling biocide grandfathered into the national antifouling registration system (Lewis 2010). Dithiocarbamate pesticides, of which thiram is one, are one of five chemicals nominated for review by the APVMA as a priority 1 on the basis of public health and worker safety concerns (APVMA 2015b). The New Zealand EPA reassessment of antifouling biocides recommended a time-limited approval of thiram, with approval to be revoked in June 2023 (EPA 2020). Thiram is not listed as an approved active substance for antifouling in the UK (HSE 2020).

Thiram is a secondary biocide in 8 of the 52 antifouling products currently approved by the APVMA (<u>Appendix A</u>).

5) Zineb

Zineb is another dithiocarbamate pesticide, primarily used as an agricultural fungicide, that was grandfathered into the national antifouling registration system. It also falls under the proposed review of dithiocarbamates by the APVMA (APVMA 2015b). The New Zealand EPA reassessment of antifouling biocides recommended retention of the approval for zineb, albeit with additional controls (EPA 2013b). Zineb is listed as an approved active substance for antifouling in the UK (HSE 2020).

Zineb is a secondary biocide in 7 of the 52 antifouling products currently approved by the APVMA (<u>Appendix A</u>).

6) DCOIT

Dichloro-octyl-isothiazolin (DCOIT), marketed under the names Seanine 211[™] or Kathon 287T[™], is a microbiocide that was the first active substance to be fully assessed and approved by the APVMA for use in antifouling paints. The New Zealand EPA reassessment of antifouling biocides recommended retention of the approval for DCOIT, albeit with additional controls (EPA 2013b). Its use in antifouling paints is also approved in the US (Ecology WA 2019) and the UK (HSE 2020) but, in the UK, it is only approved for professional use (HSE 2004).

DCOIT is a secondary biocide in 3 of the 52 antifouling products currently approved by the APVMA (<u>Appendix A</u>).

7) Zinc pyrithione

Zinc pyrithione (ZPT), marketed under the names Zinc Omadine[™] or Zinc Pyrion[™], is a microbiocide that is a common ingredient in anti-dandruff shampoos and was fully assessed by the APVMA (then the NRA) for use as an active constituent in antifouling paint products and approved in 2001 (NRA 2001). The New Zealand EPA reassessment of antifouling biocides recommended retention of the approval for ZPT, albeit with additional controls (EPA 2013b). Its use in antifouling products has been approved in the US (Ecology WA 2019) and UK (HSE 2004).

ZPT is a secondary biocide in 8 of the 52 antifouling products currently approved by the APVMA (Appendix A).

8) Copper pyrithione

Copper pyrithione (CuPT), marketed under the names Copper Omadine[™], is a microbiocide that was fully assessed by the APVMA for use as an active constituent in antifouling paint products and approved in 2005 (APVMA 2005). The New Zealand EPA reassessment of antifouling biocides recommended retention of the approval for CuPT, albeit with additional controls (EPA 2013b). Its use in antifouling products is also approved in the US (Ecology WA 2019) and UK (HSE 2020).

CuPT is a secondary biocide in 10 of the 52 antifouling products currently approved by the APVMA (<u>Appendix A</u>).

9) Dichlofluanid

Dichlofluanid, an agricultural fungicide, was approved by the APVMA for use as an antifouling biocide in 2007 (Lewis 2010). The New Zealand EPA reassessment of antifouling biocides recommended retention of the approval for Dichlofluanid, albeit with additional controls (EPA 2013b). Dichlofluanid is approved as an approved active substance for antifouling in the UK (HSE 2020).

Dichlofluanid was seen as a replacement for diuron, and three products containing the biocide were approved by the APVMA between 2005 and 2010. However, raw material supply issues subsequently prevented its use, and there are no longer any APVMA approved products that contain dichlofluanid (APVMA 2020c).

1.4.2 Antifouling biocides not yet approved by the APVMA

Research and development into new antifouling biocides continues worldwide with the objective of finding effective and more environmentally friendly products (Zainzinger 2019). The following biocides are now in use overseas, but applications for approval are yet to be submitted to the APVMA.

1) Tralopyril

Tralopyril, marketed under the name Econea[™], is promoted as a metal-free antifouling agent (Janssen 2016). US approval was granted in 2007 (US EPA 2007) and EU BPR approval in 2014 (Janssen 2016). In addition to use as a secondary biocide in copper-based paints, it has been used in combination with zinc pyrithione to offer a copper-free antifouling paint (US EPA 2019). Tralopyril was not included in New Zealand's reassessment of antifouling biocides (EPA 2013c), nor is it yet approved in the UK (HSE 2020).

2) Medetomidine

Medetomidine is a synthetic drug used as a surgical anaesthetic and analgesic (Sinclair 2003). Research and development of the substance as an antifouling agent took place in Sweden and it is marketed for antifouling use under the name Selektope[™] (I-Tech 2020). Selektope[™] acts as a barnacle repellent and is claimed to work by temporarily activating the swimming behaviour of barnacle cyprid larvae to prevent their settlement (Goldie 2015). Use of Selektope[™] has been approved in China, South Korea, Japan and South Korea (I-Tech 2020) and it is incorporated into at least eight antifouling products from the manufacturers Chugoku, Hempel, Jotun, including coatings for ocean-going vessels (Selektope 2020). The UK Health and Safety Executive recommended to the EU in 2014 that the product should be approved as an antifouling biocide (Crawl 2014).

1.4.3 Antifouling biocides not approved, or approval revoked by the APVMA

1) Organotin compounds

Annex 1 to the *International Convention on the Control of Harmful Anti-fouling Systems on Ships 2001* (IMO AFS Convention) prohibited the application to ships of antifouling systems that contained organotin compounds that acted as biocides from January 2003, and the presence of such coatings on ships after January 2008, unless sealed under a barrier coating (IMO 2005). The APVMA cancelled the registrations of all antifouling products that contained organotin biocides, effective as of 31 March 2003. The AFS Convention entered into force in September 2008 and, as of May 2020, had been ratified by 89 states representing 96% of world shipping tonnage (IMO 2020).

The AFS Convention requires that vessels greater than 400 gross tonnage (gt) carry an International Anti-Fouling System Certificate as evidence that the coating system is compliant and, similarly, vessels less than 400 gt, but of a length greater than 24 m, are required of have a Declaration on Anti-Fouling System (IMO 2005).

However, organotin compounds may still be present in underwater coating systems on:

- a) Domestic shipping in countries that are not signatories to the Convention or do not have parallel domestic regulations
- b) Small vessels in countries without domestic regulations to prevent their use. For example, one US paint company continues to advertise tributyltin-containing antifouling paints as "Export – (Non-US)" (Sea Hawk 2020). The market is understood to be countries in the Caribbean
- c) Vessels where the organotin antifouling was applied before 2003, subsequently sealed under a barrier coat, and the total system not removed and replaced since. This scenario is considered unlikely.

Dibutylin dilaurate or dibutyltin dioctanoate are commonly used in the formulation of silicone FRCs, with both acting as catalysts for the room temperature vulcanisation (i.e. curing) of the silicone (Davies 2010, Lejars et al. 2012). To allow for this, the use of an organotin <u>not acting as a biocide</u> in a hull coating is allowed by the IMO AFS Convention (Appendix to MEPC 104(49), para 6.3) up to a threshold level of 2,500 mg Sn/kg dry paint (IMO 2005). For organotins acting and released as biocides, tin concentrations of up to 50,000 mg Sn/kg occur (IMO 2005).

When introduced in the 1960s, triorganotin compounds were considered ideal antifouling biocides because of their "rapid" degradation to non-toxic compounds (Omae 2006). Degradation in the environment, caused by hydrolysis, UV light and microorganisms, involves the progressive removal of organic groups from the tin atom: e.g. tributyl to <u>di</u>butyl to <u>mono</u>butyl to inorganic tin (Seligman et al. 1996). Each step is associated with lowered toxicity; for example, dibutylin has been found to be an order of magnitude less toxic than tributyltin to mussels (Widdows & Page 1993), and the ultimate inorganic tin is considered harmless (Omae 2006). The environmental problems with tributyltin biocides were that, in areas of high input and low water exchange such as marinas and harbours, the degradation rate (half-life) was insufficient to prevent significant harmful effects to non-target species (Lewis 1998), particularly to molluscs (Lee 1996).

Unlike the biocidal organotins, in which tributyl moiety is released through the coating surface where the toxic action happens, the dibutyltin used within FRCs remains chemically bound within the paint (Akzo Nobel, 2016). Tests at International Paint in the UK found that the DBT content in a 10-year-old flake of *Intersleek* silicone FR coating was 0.4%, compared to the original content of 0.6% (C. Anderson, pers. comm.).

The presence of dibutyltin in an FRCs is not considered to be an environmental contamination issue if the coating is cleaned in-water because:

- The dibutyltin is bound within the paint by the silicone curing process and so is not released during cleaning, even if within a detached paint flake (Akzo Nobel 2016)
- The concentration of dibutyltin in the dried paint film is very low, and permissible under the AFS Convention (IMO 2005)
- Dibutyltin has low toxicity compared to tributyltin, and further degrades in the environment to even less toxic monobutyltin, then harmless inorganic tin (Seligman et al. 1996).

Reflecting the difference in toxicity, the Australian Water Quality Guidelines lists marine water trigger values for this tributyltin and does not include di- or monobutyltin (ANZECC/ARMCANZ 2000).

2) Cybutryne

Cybutryne (2-methylthio-4-tert-butylamino-6-cyclopropylamino-s-triazine), is marketed as Irgarol 1051[™], is an environmentally persistent herbicide and algaecide (Thomas 2009). An application was made to the APVMA for its approval for antifouling use in the 1990s, but this was rejected because of the emerging information on environmental persistence and toxicity. The import and manufacture of antifouling paints containing cybutryne was banned by New Zealand in 2013 (EPA 2013c), and the UK revoked approval for both amateur and professional use in 2003 (HSE 2004). Cybutryne continues to be used in antifouling paints in the US, but there have been recommendations for its prohibition (Ecology WA 2019).

In February 2020, the seventh meeting of the IMO's Sub-Committee on Pollution Prevention and Response agreed on amendments to the AFS Convention for a ban to apply or re-apply antifouling systems containing cybutryne from July 2022, and for removal or sealing such coatings applied before this date either before July 2027 or no later than 60 months following the application of such coating prior to July 2022 (DNV-GL 2020).

3) Chlorothalonil

Chlorothalonil is an agricultural fungicide and has been used as a microbiocidal preservative in paints and adhesives (Amaras et al. 2018). It is currently listed by the APVMA as nominated and prioritised (Priority 2) for review because of environmental, human health, and environmental residue concerns (APVMA 2015b). As an antifouling biocide, it was grandfathered into the national antifouling registration system (Lewis 2010) but is no longer present in any APVMA approved antifouling products (Appendix 1). The UK revoked approval of its antifouling use by both amateurs and professionals from 2003 (HSE 2004), and New Zealand banned the import and manufacture of antifouling paints containing chlorothalonil from 2013 (EPA 2013c).

4) Mancozeb, ziram, tolyfluanid, octhilinone

None of these substances is present in antifouling products approved by the APVMA (Appendix 1). Mancozeb and ziram are dithiocarbamate pesticides and are thus included in the nomination for review of these pesticides by the APVMA as a priority 1 based on public health and worker safety concerns (APVMA 2015b). Recommendations from the New Zealand EPA reassessment of antifouling biocides were to retain approval of mancozeb and tolyfluanid with additional controls, and to ban products containing octhilinone or ziram (EPA 2013b).

Tolyfluanid continues to be listed as an approved active substance for antifouling in the UK (HSE 2020).

1.5 Non-active coating constituents

In addition to active constituents, antifouling products contain non-active constituents that include binders, pigments, extenders, solvents and additives (APVMA 2020). Some of these constituents have metal atoms within their structures and could be released into the environment by passive release as part of the coating hydration or hydrolysis process.

1.5.1 Binders

Self-polishing copolymers developed to replace TBT-copolymers include zinc, copper and silyl acrylates. These copolymers hydrolyse in seawater to release the metal ion group and leave the water-soluble polymer backbone (Bressy et al. 2009). The level of copper or zinc released is insufficient to confer any antifouling effect (Shilton 1997), which is generated by the added copper and secondary biocides released from the coating as the surface polishes.

1.5.2 Pigments

Pigments are often metallic compounds and can include oxides of zinc, iron and titanium. Zinc oxide is a common additive to antifouling paints, but not as a biocide. It can have multiple functions: to regulate paint dissolution, to stabilise wet paint in the can, to modify dry film properties, and as a pigment (IPPIC 2012).

1.5.3 Plasticisers

Dibutyltin dilaurate is used as a catalyst for curing silicones, as a stabiliser for polyvinyl chloride resins, as a corrosion inhibitor and, in veterinary use, to treat tapeworms in chickens (Blunden & Chapman 1986, OSHA 2003). Dibutyltin diacetate is used as a catalyst for the crosslinking of silicon/rubber sealants (Davies 2010). Both of these low toxicity organotin compounds can be used as catalysts in the curing agent for silicone fouling release coatings (Lejars et al. 2012). To allow for such use, under the AFS Convention, an antifouling paint is allowed a maximum

content of 2500 mg Sn/kg dry paint, and the levels in fouling release coatings are below this (IMO 2005).

1.6 Uncoated metallic surfaces

Although most underwater surfaces of a vessel are painted, for operational reasons, some specific areas are not.

1.6.1 Cathodic protection anodes

Cathodic protection (CP) systems are installed on metal hulled vessels, to the outer hull and also in seawater tanks, to prevent penetrative corrosion of the structural metal if the coating system is breached and seawater is able to contact the metal substrate (Rolands & Angell 1976). Cathodic protection systems are either impressed current (ICCP) systems, in which an electrical potential difference between the hull and a reference anode is balanced by output from the ICCP anode, or sacrificial anode systems, in which galvanic anodes of a metal less noble (more reactive) than the structural material are attached to the hull (Rolands & Angell 1976). If metal substrate is exposed, the anode will preferentially corrode instead of the structural metal. Sacrificial anodes on ships are made of alloyed zinc (for iron, steel and aluminium) or aluminium (for iron and steel) (Morgan 1987). Zinc is the traditional material used, but aluminium anodes are lighter, can last longer, and can provide better protection (MME 2020). The zinc alloy used for anodes can contain 0.025 to 0.15% of cadmium (Standards Australia 2016).

1.6.2 Propellers

Conventionally propellers are not painted which, at least in part, is because of the rapid erosion and loss of the paint system from the propeller surfaces by water turbulence and cavitation, and for vessels operating in shallow waters, abrasion by disturbed sediment. However, recently, silicone FR coatings in combination with a high performance anti-corrosive coating system are proving to be durable, to reduce biofouling, and to minimise the need for propeller polishing (Atlar *et al*, 2002, Korkut and Atlar, 2012)

Propellers are mostly constructed from copper and steel alloys, and traditionally from nickel aluminium bronze or manganese aluminium bronze alloys (Vardhan et al. 2019). Nickel aluminium bronze can contain, for example, around 80% copper, 10% aluminium, 5% nickel and 4% iron (Powell & Webster 2012).

1.6.3 Sensor windows

Depth and other sensor and transducer windows are also not painted but are constructed on non-metallic plastics or composites, for example polycarbonate (RD Instruments 2002).

1.7 IWC Recommendations

In regard to hull coatings and surfaces, the following recommendations are made with respect to IWC. Hull grooming and proactive or reactive IWC should not:

- be permitted if the vessel does not have a valid International Anti-Fouling System Certificate or Declaration on Anti-Fouling System that lists biocides present in the coating
- be permitted if the AFC contains diuron, cybutryne, ziram, chlorothalonil, or other biocides restricted or banned elsewhere in the world.

2 Contaminant sources

2.1 Coatings

The process of biofouling development starts with the adsorption of a film of organic and inorganic matter from the seawater, followed by microbial colonisation of this film by bacteria, microalgae and protozoans. This occurs on all surfaces, whether non-biocidal or biocidal. On biocidal coatings, bacteria and microalgae often exude polysaccharides or other substance (slime) that ameliorate the toxicity of the biocide to the microbes. On non-biocidal surfaces, several days to weeks after first immersion, multicellular organisms will settle, attach and grow. An effective antifouling coating will hold the biofouling development at the biofilm stage until the biocide release rate drops below that necessary to prevent macrofouling attachment.

On biocide-free coatings or surfaces, macrofouling development is largely unconstrained but, for fouling release coatings, the strength of adhesion is reduced, and organisms can be dislodged by turbulent water movement across the surface, or light mechanical force.

Once a biocidal surface is immersed, biocide release will commence through the process of hydrolysis or hydration at the coating surface (Bressy et al. 2009). This changes the surface composition of the coating and three different layers develop: the innermost sound layer of unreacted paint, the leached layer from which biocide has dissolved but the skeletal paint matrix remains, and the surface biofilm of microbes and their extracellular exudates (Morrisey et al. 2013)

Three types of IWC can be defined: hull grooming, proactive cleaning, and reactive cleaning.

Hull grooming is regular cleaning to remove the biofilm, surface deposits, and friable surface from hull surfaces to reduce surface microroughness and viscous drag. The benefit of hull grooming cleaning is improvement in ship performance and efficiency which reduces environmental impact by reducing drag, fuel consumption, greenhouse gas emissions and costs. It will also eliminate the need for high intensity hull cleaning methods and can increase coating longevity. Hull grooming is generally restricted to the planar surfaces of the hull that are prone to hydrodynamic drag. Propeller polishing can be considered similar to hull grooming, as it is undertaken to restore the propulsion efficiency of propellers.

Proactive IWC is the removal of early stages of biofouling to prevent the growth and maturation of macrofouling organisms, on both hull surfaces and on and within hull niches that, if established, can significantly impact on vessel efficiency and facilitate marine species translocation. Reactive IWC is the removal of established macrofouling to restore hull efficiency or remove growth considered to pose a biosecurity risk.

Hull grooming and proactive IWC are similar in removing the surface biofilm and, if present, the early, microscopic stages of newly settled macrofouling, and some or all of the leached layer. Reactive IWC removes hard and soft macrofouling, together with underlying and interspersed biofilm, and friable leached layer. If aggressive cleaning methods are used for proactive or reactive IWC, the outer surface of sound paint underlying the leached layer may be removed. Paint flakes may also be removed during IWC if the paint system is damaged or defective.

Biocide concentrations are higher in sound paint and paint flakes than in the leached layer and/or biofilm.

2.1.1 Sound paint

The base layer of the active antifouling coating is the sound layer where seawater has yet to penetrate to commence the hydrolysis/hydration reactions. This layer will have the same composition and biocide content as the dried paint film prior to immersion.

2.1.2 Leached layer

The mechanism of biocide release from an antifouling coating results in a surface layer that is depleted of biocide and other soluble compounds (Lewis 1998). In soluble matrix and SPC coatings, this is due to the biocide dissolving at a faster rate than the dissolution or hydrolysis of the paint matrix (Lewis 1998). The area of biocide depletion is termed the 'leach' or 'leached' layer. The thickness of the leached layer varies with the length of immersion and water velocity across the coating surface, but also between coating types with, generally, insoluble matrix coatings developing 'thick' leached layers (\sim 75+ µm thick), soluble matrix/ablative coatings 'relatively thick' layers (30 – 80 µm), and tin-free SPCs thinner layers (10 – 40 µm) (Morrisey et al. 2013).

2.1.3 Biofilms

Antifouling and fouling control coatings are all rapidly colonised by bacteria and other microorganisms which develop surface biofilms (commonly referred to as 'slime') (Cassé & Swain 2006). The composition of this biofilm changes with time: the first colonisers are small bacteria, followed by larger bacteria and diatoms (Lewis 1998). Diatoms contribute much of the biomass of biofilms on illuminated surfaces (Molino et al. 2008). Stunted and prostrate filamentous algae can also establish within the biofilm (Taylor & Evans 1976, Woods et al. 1988). The biofilm is also highly absorptive and, although microorganisms and their remains form the most conspicuous components of the film, varying amounts of extracellular polymeric substances (EPS), trapped detritus, inorganic precipitates, and corrosion products form the bulk of the layer (Lewis 1998). Measured thicknesses of biofilms range from 0 – 600 μ m (Jackson & Jones 1988), but measurements on one vessel coated with an insoluble matrix paint ranged between 1,500 and 2,500 μ m (Doi 1982). EPS in biofilms can modify the release of biocide from the coating surface and trap and bind copper ions (Lindner 1988, Yebra et al. 2006).

2.1.4 Paint flakes

Lifting and flaking paint can be the result of paint system defects and failures, or mechanical damage (Fitzsimons 2011). The overall chemical composition of a flake will depend on the depth of the fracture layer within the coating system. If delamination is at the hull surface, the flake will include all coats of the anticorrosive system, any tie or barrier coats, and the antifouling topcoats. If the system has been recoated at a dry-docking without removal of the existing system, then the coats of new barrier/tie/antifouling paints will also be present in the flake. If the fracture layer is within the system, which can be due to surface contamination during overcoating, the flake will be composed of whatever coats were applied above the delamination surface.

Paint lifting or delamination often indicates system breakdown, poor surface preparation for painting, or poor paint application (Fitzsimons 2011). These failures can compromise the

performance of both the anticorrosive and antifouling function of the paint and, mostly, can only be rectified by repair, renewal, or replacement in a dry-dock.

2.2 Unpainted metals

Most metals will corrode when immersed in seawater (Powell 2012), but at varying rates (Francis 2012). The antifouling effect of copper and cupro-nickel alloys is, for example, known to be due to the slow release of copper from the metal surface (Redfield 1952). Released copper ions can react to form insoluble copper precipitates on the metal surface, one example being a green copper patina of basic copper chloride (Lindner 1988). This patina can also form on copper-based antifouling paints, particularly in the splash zone along the wind and water line of a vessel (Lindner 1988).

Sacrificial CP anodes are designed to corrode, the more defects in the paint system and exposed hull plate, the faster the anodes will erode (Rolands & Angell 1976). If the hull coating is in excellent condition, the anode will not corrode. Similarly, to antifouling paints, the corrosion process can result in friable corrosion products on the anode surfaces, but the unreacted metal will be sound (Bohnes & Franke 1997).

3 Source contamination

3.1 Biofilms

Surface biofilms can accumulate biocide released from the paint (Lindner1988, Yebra et al. 2006). Slimes on organotin SPC coatings were often thicker than those on copper-based paints, as biocide-tolerant diatoms secreted large quantities of extra-cellular mucilage, which bound to TBT and acted as a protective mechanism (Thomas & Robinson 1986, Callow 1990). High levels of TBT were therefore present in these biofilms (Fent & Humm 1995, Fletcher & Lewis 1999). As discussed in Section 1.4.1 in copper-based paints, the unstable and toxic cuprous ion rapidly oxidises to the cupric ion when released and this, in turn, complexes with organic and inorganic ligands. The loosely adherent biofilm can be removed by wiping or light cleaning, but the copper accumulated in this biofilm would be in a non-toxic complexed form.

Published information on the levels of biocide in biofilms, or information that infers biocide levels, is scant (Morrisey et al. 2013). For cuprous oxide, available information did enable an estimation for use in modelling environmental discharges from in-water cleaning (Morrisey et al. 2013). For this modelling, the estimate of copper concentration in the biofilm was 2.5 μ g Cu/cm³, and the copper removed with slime between 25 and 100 μ g/cm²/event. The copper content of the biofilm since measured on one vessel as part of an in-water cleaning trial in 2015 was [0.02-] 0.18 [-1.5] μ g/cm², which is much lower than the estimates used in the Morrisey et al. modelling (GRD Franmarine Holdings Ltd, unpublished data). The percentage of copper in particulate form (i.e. non-toxic) in these biofilm samples was also high (~75-80%)

3.2 Primary and secondary fouling

In addition to a biofilm, vessels may accumulate secondary fouling includes macroscopic sessile organisms, visible to the naked eye, that are attached directly to the substrate, or tertiary fouling which includes macroscopic sessile or mobile organisms growing on or in interstices between the secondary biofouling organisms.

The literature does not provide any evidence of released biocide accumulating in secondary or tertiary biofouling. Biocide present in the biofilm is not accumulated by the microorganisms, but by sequestration into the extracellular slime because of, in the case of copper, the complexation of the copper ions with the organic ligands in the slime (Brooks & Waldock 2009a). Bound copper is not considered to be bioavailable (Thomas & Brooks 2010).

The uptake of copper and other trace metals by multicellular organisms can be by absorption from solution across a permeable body surface (e.g. the gills) or from food via the alimentary canal (Luoma & Rainbow 2008). Distinct from this is adsorption onto the surface of the organism. The adsorbed copper has no ecotoxicological role within the organism involved (Luoma & Rainbow 2008). Any bioaccumulation in secondary/tertiary biofouling could therefore be by absorption of dissolved copper across the gills, or via the gut from contaminated food or particles filtered from the water column by organisms during filter feeding. Free copper is rapidly bound on release from the coating, minimising the likelihood of bioaccumulation in biofouling organisms, it is more likely a consequence of heightened environmental contamination, to which antifouling may contribute, but the route is indirect. Bioaccumulation in

biofouling organisms attached to a hull would be presumed to have lower levels of contamination than those growing on fixed structures within a contaminated port or harbour, due to the shorter or intermittent exposure time of the former.

If secondary or tertiary fouling is present on a surface, then it can be inferred that release of the biocide from the hull coating is of an insufficient level to prevent biofouling attachment and further reduce any risk of significant accumulation within an organism. For these reasons, and because any copper absorbed by an organism would be chemically bound in a non-toxic form (Luoma & Rainbow 2008), secondary and tertiary biofouling removed during IWC is not considered to pose any measurable chemical contamination risk.

3.3 Leached layer

The leached layer is likely to be a physically unstable layer, due to the dissolution of biocide and other more soluble paint constituents, so would be removed by moderate cleaning pressure. When in dry-dock, surface preparation of existing coatings prior to recoating requires high pressure (~1500 psi) water washing to remove the dried slime and leached layer to ensure adhesion of the new paint (ABS 2007). The leached layer is likely to be softer when hydrated before aerial exposure, but removal in-water may still require more than a light wipe, particularly if insoluble copper precipitates have formed. However, removal of the biofilm and leached layer is important to rejuvenate a coating and re-establish optimal biocide release rates.

The only known published information on the concentration of biocides in the leached layer is that inferred in Morrisey et al. (2013) from SEM/EDX traces through antifouling paint flakes and from measurements of copper content in vessel wash down water. Values of $2.4 - 24 \ \mu g \ Cu/cm^2$ were applied in the Morrisey et al. modelling. Along with the biofilm, actual measurement of the copper content of the leached layer was undertaken as part of the in-water cleaning trial in 2015 (GRD Franmarine Holdings Ltd, unpublished data). The measured concentration range was [0.02-] 1.02 [-8.7] $\mu g \ Cu/cm^2$, very much at the lower end of the range applied by Morrisey et al. The percentage of particulate copper was higher than for the biofilm: ~85-95%.

3.4 Sound paint

The sound paint below the leached layer contains the highest concentrations of biocide, equivalent to that in the dried paint film when applied. Aggressive cleaning, for example using steel bristled brushes, can cut into and remove sound paint.

The concentration of biocide in sound paint can be calculated from the per cent volume of the biocide in the wet paint, and parameters such as the per cent solids in the wet paint, the dry film/wet film thickness ratio, the specific gravity of the wet paint, and the weight fraction of active ingredient in the biocide (Finnie 2006). For antifouling products approved for use in Australia, the biocide content is publicly available via the APVMA Public Chemical Registration Information System. The other parameters needed for the calculation are usually provided on the technical or product data sheet for the product.

3.5 Paint flakes

The biocide content of a paint flake is dependent on the surface area of the paint flake and the number, composition and thickness of paint layers within the flake. When a flake is deposited in the environment, the release of biocide is only from exposed surfaces of the paint, so the top face

of the flake, from around the edge, and from the lower face if disbondment has occurred at the antifouling/anticorrosive paint interface. The flake will persist in a calm environment and only degrade at the rate that an equivalent surface area of paint would degrade while on a coated substrate (Takahashi et al. 2012). However, if the flake is in a turbulent environment, particularly one with mobile sand, gravel or other abrasive material, the flake is likely to be physically broken down and the total biocide content of the flake released into the environment (Turner 2010).

Dislodged paint flakes that fall to the sea floor to become incorporated into the sediment can directly contaminate the sediment as paint flakes or particles, and also through indirect contamination via biocide dissolution and subsequent adsorption (Turner 2010, Soroldoni et al. 2020). Flakes deposited in the sediment, even if not broken down, can skew measurements in environmental monitoring or sediment toxicity assessment required by the National Assessment Guidelines for Dredging (CoA 2009). The recommended method for bulk sediment chemical analyses in these guidelines is for the sample to be ground to ensure homogeneity followed by, for the analysis of non-volatile metals, strong acid extraction. This would dissolve any paint flake and release all copper or other metals within the flake into the test sample.

In-water cleaning is likely to dislodge loose or lifting paint, or break blisters on a degraded system but, if the coating system is sound, should not cause damage that results in paint flakes.

Paint flakes generated during hull maintenance activities would be representative of the full coating system, so could include primer, anticorrosive, sealer and tie coats in addition to the antifouling paint. As the overall concentration of biocide in a paint flake is an average over all paint layers, the measured value would often be less than the concentration in the antifouling paint alone. For some other metals, including zinc and aluminium, the concentration may actually be elevated in a coating system sample because of the use of these metals in anticorrosive coatings.

No information was found by Morrisey et al. (2013) on the quantity of paint flakes likely to be dislodged during in-water cleaning, but this was considered likely to vary with the condition and integrity of the coating system. If the in-water cleaning is part of hull husbandry to remove slime and light macrofouling to improve hull efficiency, or to reactivate a paint coating by removing the leached layer, then the extent of paint breakdown and delamination was expected to be low (Morrisey et al. 2013).

If breakdown is extensive, there is also likely to be well developed biofouling, as the system would be at or close to its service life. In this latter situation slipping or dry-docking for antifouling renewal should be the recommended treatment, rather than in-water cleaning (DoE/NZMPI 2015).

If silicone fouling release coatings are recoated without suitable and thorough cleaning of the existing coating, the newly applied coating can delaminate. Although these coatings are biocide free, the coatings are elastomers which are pliable plastics. Flakes are therefore a form of plastic pollution and release into the marine environment should be avoided.

3.6 IWC Recommendations

In regard to source contamination, it is recommended that:

IWC should:

• capture and contain paint waste if the coating system is defective and paint flakes are likely to be removed during cleaning

IWC should not:

- damage the coating
- cut deeply in to sound paint below the leached layer
- be undertaken if there is extensive significant coating system breakdown with flaking or lifting of the paint. The vessel should, instead, be dry-docked for coating system repair, renewal or replacement.

4 Cleaning scenarios

4.1 Grooming & cleaning

Three types of IWC can be defined: hull grooming, proactive cleaning, and reactive cleaning.

Hull grooming is regular cleaning to remove the biofilm, surface deposits, and friable surface from hull surfaces to reduce surface microroughness and viscous drag. The benefit of hull grooming is improvement in ship performance and efficiency which reduces environmental impact by reducing drag, fuel consumption, greenhouse gas emissions and costs. Regular grooming may also eliminate the need for high intensity hull cleaning methods and can increase coating longevity. Hull grooming is generally restricted to the planar surfaces of the hull that are prone to hydrodynamic drag. Propeller polishing can be considered similar to hull grooming, as it is undertaken to restore the propulsion efficiency of propellers.

Proactive IWC is the removal of early stages of biofouling to prevent the growth and maturation of macrofouling organisms, on both hull surfaces and on and within hull niches, which, if established, can significantly impact on vessel efficiency and facilitate marine species translocation. Reactive IWC is the removal of established macrofouling to restore hull efficiency or remove growth considered to pose a biosecurity risk.

Hull grooming and proactive IWC can be considered similar in their approach, with a focus on removing the surface biofilm and, if present, the early, microscopic stages of newly settled macrofouling, and some or all of the leached layer. Reactive IWC removes hard and soft macrofouling, together with underlying and spatially interspersed biofilm, and friable leached layer. If aggressive cleaning methods are used for proactive or reactive IWC, the outer surface of sound paint underlying the leached layer may be unintentionally removed.

4.1.1 Hull grooming

Hull grooming is a relatively new concept that aims, by regular, light cleaning to proactively remove microbial biofouling and newly settled macrofouling and therefore maintain coatings on the hull and laminar surfaces smooth and free of secondary biofouling (Tribou & Swain 2010). The intent of hull grooming is to maintain a light biofilm layer to consequently improve ship performance and efficiency, and to minimise environmental impacts by reducing drag, fuel consumption, greenhouse gas emissions and costs (Hunsucker et al. 2018). Grooming can also, by controlling macrofouling, minimise the risk of spread of invasive marine species, increase coating longevity, and eliminate the need for high intensity hull cleaning methods, (Tribou & Swain 2010, Hearin et al. 2015, 2016,).

Trials have assessed weekly and monthly grooming frequencies on static test panels (Tribou & Swain 2017) and, although both were effective, the optimum grooming frequency is still to be determined (Swain 2019). Although the work of Tribou and Swain is directed toward maintenance practices for US Navy ships, the commercial application of grooming is likely to be on owner-operated, active deep sea trading vessels and cruise ships where hull efficiency and fuel economy is of operational importance. Grooming is likely to be performed on an opportunistic basis, with the frequency dependent on the operational schedules. The newly developed "Hull Skating Solutions" released by Jotun is such an application (Jotun 2020).

The optimum frequency for grooming would likely be based on the coating type, the operational profile of the vessel, and the operational environment (Swain 2019). The earlier the cleaning is completed in the process of biofouling development, the less likely will be the requirement for biological waste capture. Monitoring ship performance provides an indicator of increasing hull friction and can be used as a guide to the need for grooming. From an environmental perspective, the more often a hull is groomed the better, to prevent biofouling-induced increases in fuel consumption and consequent harmful air emissions. However, this needs to be balanced against any accelerated erosion of the AFC.

4.1.2 Reactive IWC

Reactive IWC is undertaken to remove established macrofouling. Before advent of the organotin self-polishing coatings in the mid-1970s, antifouling coatings generally lost effectiveness in less than 12 months and hulls were often scrubbed with brush carts to remove biofouling, and the insoluble surface precipitates, to improve ship performance and extend the dry-docking interval (Bohlander 2009). This practice has continued, for example on US Navy ships (NSSC 2006).

1) Hull surfaces

Until recently, the focus and intent of hull cleaning has been to improve the hydrodynamic performance of a vessel by removing established biofouling and rejuvenating the antifouling coating. Hull surfaces, including both the vertical sides and the flat bottom, were the areas of concern and brush carts were employed as the most economical method in terms of both cost and time (Bohlander 2009).

2) Propeller polishing

Across the shipping industry, propeller cleaning has been a more common practice than hull cleaning. Propellers are generally not painted with biocidal coatings and the added roughness caused by the establishment of hard-shelled biofouling and calcium deposits on the propeller blades, cavitation and corrosion of the blade surfaces negatively impacts engine operation, propulsion, and fuel efficiency (Atlar et al. 2002, Carlton 2019). The aim of polishing is to proactively remove surface roughness, and this is achieved, both in and out of the water, using power tools fitted with rotating discs or brushes (Morrisey & Woods 2015). The frequency of propeller polishing varies, with suggestions that best practice for commercial ships is every 6 months (Hydrex 2012).

3) Niches

Until relatively recently, the driver for any in-water cleaning of ships has been the impact of marine growth on operational performance, and this also applies to hull niches. The two major niches of concern to a ship's operation are sea chest grates and through-hull sensors. The clogging of sea chest grates reduces water flow into the sea chest, and on into the pipework of cooling and other inboard systems. For cooling water systems, reduction of water flow can reduce the effectiveness and cause failures of heat exchange coolers, resulting in engine or other critical system breakdowns. Marine growth on depth, speed, ICCP and other through hull sensors can compromise performance. Cleaning of both sea chest grates, and sensor surfaces would be by divers using simple hand tools, such as scrapers, or high-pressure water jetting.

Other niches have been designed to accommodate the marine growth that may develop between dockings to avoid impacts on operational performance. Sea chests, for example, are designed with a large internal volume and cross section, much greater than the cross section of the intake pipe or pipes drawing water through the sea chest. Large aggregations of marine growth can

therefore develop on the inner walls of a sea chest without a reduction of the critical flow into inboard piping system. For this reason, sea chests have become a niche of concern in regard to biosecurity (Coutts & Dogshun 2007, Frey et al. 2014).

Removal of growth from a sea chest in-water requires the opening or removal of the sea chest grate, some of which are secured by welds. The sea chest opening, and internal dimensions, then need to be sufficient to enable diver access. Some sea chests are sufficiently large and internally open to enable this but, for many, the opening may be too small, the chest too small, there may be baffles internally dividing the internal chest or, if box coolers are fitted, and access around the cooler is limited. As with the design of sea chests to accommodate biofouling, consideration of access for cleaning has also not seemed to be a design priority.

4.1.3 Cleaning methods

1) Manual

Manual removal of biofouling by divers is undertaken with hand-held scrapers, small hand-held power tools, such as hydraulic rotating brush or disc units, or high-pressure water jetting systems (Morrisey & Woods 2015). Manual scraping is a targeted cleaning method commonly used to dislodge scattered barnacles off hulls, or the removal of secondary and tertiary biofouling from niche areas. Water jetting is often used in conjunction with scraping to clean difficult to access areas, such as in rudder hinges, under rope guards, inside sea chests if the grates are unable to be removed, etc. Water jetting can also more effectively remove soft fouling mats, such as green algal bands along the waterline.

2) Mechanised

Broad areas of hull plate on the vertical sides and flats of ships can be cleaned by 'brush carts', which have one or more rotating discs or high-pressure water jets under a steerable motor housing (Bohlander 2009, Morrisey & Woods 2015). These brush carts are held against the hull by suction forces or by magnets. Globally, most systems do not have the capability to contain and capture cleaning debris (Morrisey & Woods 2015). However, some systems able to do this are now operating or under development (Lewis 2013, Subsea World News 2019, The Maritime Executive 2019, Tamburri et al. 2020).

Most brush carts are hydraulically powered and steered and controlled by a diver, however some autonomous hull cleaning units have been developed and are now in operation. These are tethered units that are controlled from the surface through an umbilical. Untethered, remotely operated units are under development, primarily for hull grooming (See Morrisey & Woods 2015 for examples of these three systems).

a) Non-contact

Non-contact rotary disc systems have blades, or brushes, that do not touch the hull surface. The biofouling is removed by the water turbulence created by the spinning discs (Morrisey & Woods 2015). High pressure water jetting systems also do not have direct physical contact with the surface. FR coatings, in particular, need to be cleaned with non-contact methods due to the susceptibility of these coatings to abrasion damage and scratching (Lewis 2013, Oliveira & Granhag 2020).

b) Non-abrasive

Non-abrasive rotary disc systems use brushes with soft silicon polypropylene or nylon bristles. These are able to remove light fouling, macroalgae and slime, but not heavy, strongly adhered growths of hard-shelled organisms, such as barnacles and oysters.

c) Abrasive

For the removal of medium to heavy fouling, for example barnacles, tubeworms and mussels, brushes with wire or stainless-steel bristles are needed.

4.2 Cleaning contaminant levels

4.2.1 Manual cleaning

1) Hand scraping

The use of hand scrapers can remove visible biofouling and possibly some of the coating surface. If areas of soft biofouling, such as patches of filamentous green algae, are removed by hand scraping, it is possible that some of the coating surface will be removed but, if the coating is in good condition, this is likely to be the leached layer and not the harder underlying coating. Should the coating be breaking down, with the biofouling on or around areas of delaminated antifouling coating, hand scraping could dislodge flaking or lifting paint in the area being cleaned.

Hard shelled biofouling organisms attached to hull surface are mostly strongly adherent, and often the adherent base cannot be removed (personal observation). This is particularly the case for acorn barnacles with a calcareous baseplate and, on sound paint, the base persists after removal of the body and wall plates. The lower valve of oysters is similarly strongly adherent and difficult for divers to remove. A white calcareous scar often remains after tubeworms are removed, but this is a light residue compared to barnacles and oyster bases.

The entire shells of barnacles and oysters, including the base plates and lower valves, can be removed if the surface of the paint is not sound. This can happen if there is a well-developed leach layer, or if the coating system is defective or structurally weak and inter-coat or base coat delamination occurs. In the latter case, a flake of paint adhering to the barnacle or oyster may be removed. If dislodgement is due to a friable leach layer, little coating is likely to detach, and this coating residue would most likely be biocide depleted. Barnacles, oysters and other hard-shelled organisms should lift cleanly from a fouling release coating with no coating damage (Lejars et al. 2012).

2) Powered hand tools

On painted surfaces, the degree of coating removal will depend on the aggressiveness of the clean. This will be discussed below under mechanical cleaning.

No contaminants are likely from the removal of biofouling from unpainted propellers. However, if the propeller roughness is due to corrosion pitting of the blade surfaces then, to achieve a smooth surface, the peaks of metal roughness need to be removed which would generate metal particles. Metal particles are likely to sink to the seafloor where corrosion reactions would continue.

4.2.2 High pressure water jetting

The effect of high-pressure jetting on a surface would depend on the water pressure at the nozzle and the distance between the nozzle and the surface. Due to the resistance of the water,

when this is performed underwater the drop in pressure between the nozzle and the surface is greater than in air.

In dry-dock, high pressure water jetting is used to remove light fouling, slime and other surface deposits, and the leached layer to reactivate the antifouling, if it is not to be recoated, or as surface preparation to ensure good adhesion of new paint coats. If the nozzle is held too close to the paint surface, directed directly at the surface, and/or held in one position for too long, the water jet will cut into the sound paint below the leached layer. This can still happen under water but, because of the resistance of the seawater, the risk is reduced. In the hands of a skilled operator, or for automated cart systems, no more than the slime and leached layer is likely to be removed.

As for all cleaning methods, if there are coating defects that have led to areas of flaking or lifting paint, water jetting will dislodge paint flakes from the surface.

4.2.3 Mechanical cleaning

1) Non-contact

Non-contact mechanical cleaning methods can remove slime and weakly attached macrofouling, both soft and hard. The leached layer of biocidal antifouling coatings would only be removed if this is loosely adherent. Flakes of loose and lifting paint from defective areas of paint are likely to be dislodged.

2) Non-abrasive

Non-abrasive cleaning, with soft brushes, can remove slime, weak to moderately strongly attached macrofouling, both soft and hard, and the leached layer. Strongly adherent biofouling, such as calcareous barnacle bases and lower valves oysters, are unlikely to be removed. Non-abrasive cleaning may not be able to completely remove thick fouling growth, whether dense aggregations of barnacles or calcareous tubeworms, or complex aggregations of hard and soft fouling. Non-abrasive methods should not remove sound paint. Loose and moderately adherent lifting and delaminating paint flakes are likely to be dislodged.

3) Abrasive

Abrasive cleaning can remove all hard and soft growth, slime, the leached layer and, most likely the outer surface of sound paint. The depth of coating removal would depend on the hardness and density of the brush bristles, application pressure and the transit speed of the cart across the surface. Delaminating and blistering paint would be removed, with the likelihood of flakes being dislodged out from the location of initial delamination. Cleaning can also aggravate the spread of corrosion by rupturing blisters, if present, at the coating-steel interface.

4.3 IWC Recommendations

In regard to cleaning scenarios, it is recommended that:

IWC should:

• be restricted to areas on wetted surfaces where growth is considered unacceptable to vessel operators or for biosecurity compliance, and the least aggressive and most appropriate methods used to achieve the required result. The cleaning method should be chosen to ensure the coating is not damaged. A combination of methods is likely to be required for the outcome of a 'clean hull', which includes all wetted surfaces.

Less restrictive regulations for hull grooming would assist with uptake of this approach to minimise the development of primary biofouling that can increase hull friction and consequent fuel consumption and harmful air emissions. A method is proposed for this in Section 7. Similarly, facilitating proactive IWC, would minimise the need for reactive IWC.

5 Cleaning & capture requirements

5.1 Effluent standards

The current 'Anti-Fouling and In-Water Cleaning Guidelines' (DoA/NZMPI 2015) recommend that, for contaminant discharges, the "contaminant discharges must meet any local standards or requirements". However, Australian Government, State or Agency regulatory standards that are directly relevant to discharges from IWC systems have not been identified.

Satisfying authorities that contaminant discharges from IWC are acceptable has proven to be difficult due to the absence of any clear standards or limits for contamination concentrations in discharges. Comparisons have been drawn with trigger values in the Australian and New Zealand Guidelines for Marine and Freshwater Quality (ANZECC/ARMCANZ 2000), which were calculated at four different species protection levels, 80%, 90%, 95% and 99%. These percentages signify the percentage of species expected to be protected at each trigger value; the lowest level is applied to highly disturbed environments, such as harbours, the highest to high value conservation areas. However, these trigger values were developed with respect to concentrations in the environment, not in discharges or other inputs into the environment. Dilution of a discharge on release into a receiving water body would lower the contribution of the contaminant to the environmental concentration. The extent of dilution would depend on the volumes of both the discharge and the receiving environment.

5.2 Passive leaching

5.2.1 Biocide release rates

For biocidal antifouling coatings to be effective, the biocide must be continuously released at the surface of the coating at a concentration that will prevent the settlement and/or survival of fouling organisms (Lewis 1998). The rate at which antifouling biocide passes through the antifouling coating/seawater interface is termed the biocide leaching or release rate. This is generally expressed as the mass of biocide, in micrograms, released from a square centimetre of antifouling coating in one day (μ g biocide/cm²/day). Biocide release rates from antifouling coatings can vary with environmental variables (pH, temperature, salinity, water movement over the surface and copper concentration in the water) (Yebra et al. 2004) and also, during service, over the life of the coating system, on the formulation and the environment, and on differences in berthing locations, operating schedules, vessel speed, length of service, and condition of paint film surface (Thomason 2010).

Numerous methods have been used to attempt to quantify release rates and to determine the critical release rates for biofouling prevention (Morrisey et al. 2013). Measuring the release on a hull *in situ* has only been successfully achieved by the US Navy "dome method", with other methods either in laboratory set ups, or destructive analysis of field panels. For cuprous oxide, the conclusion that can be drawn from studies over the past 60+ years is that the minimal rate of copper release to prevent biofouling is $10 \ \mu g \ Cu/cm^2/day$, which is the rate required when a vessel is stationary in harbour (Morrisey et al. 2013).

The method for calculating biocide release rates that is now accepted by regulatory agencies, including the APVMA, is by mass-balance calculation (ISO 2010). This method is based on a simplified generic empirical model of biocide release. The inputs to the model are the specified

service lifetime of the paint (months), the amount of biocide in the coating formulation (% by weight), the weight fraction of the active ingredient in the biocide, the volume solids of the wet paint (%), the specific gravity of the wet paint, the dry film thickness of the specified paint applied for the specified lifetime (μ m), and the fraction of active ingredient in the dry film released during the specified lifetime of the paint (Finnie 2006). Finnie recommended that, if copper release rates calculated by the mass-balance method are to be used for environmental risk assessment or regulatory purposes, the calculated values need to be divided by a correction factor of 2.9.

5.2.2 MAMPEC modelling

MAMPEC (Marine Antifouling Model to Predict Environmental Concentrations) is an integrated hydrodynamic and chemical fate model, originally developed to predict environmental concentrations for the exposure assessment of antifouling substances (van Hattum et al. 2017). The model, adopted by the OECD, predicts concentrations of antifouling biocides in generalised "typical" marine environments, including harbours, marinas and the open sea, from the input of emission factors (e.g., biocide leaching rates, shipping intensities, residence times and ship hull underwater surface areas), compound-related properties and processes, and hydrodynamics related to the specific environment. The model has been validated for a number of compounds and has been recognised by regulatory authorities in the EU, other OECD countries, the USA, Japan, New Zealand and Australia (Gadd et al. 2011, van Hattum et al. 2016, APVMA 2020b). In Australia, the APVMA accepts MAMPEC modelling for the environmental risk assessment of new antifouling products submitted for approval (APVMA 2020b). Default values for 10 common antifouling biocides are included in the MAMPEC database.

For the approval of antifouling paints for boat hulls in Australia, guidance for environmental assessment involves the comparison of the Predicted Environmental Concentration (PEC) for biocides released from a particular antifouling product with the Regulatory Acceptable Concentration (RAC) (APVMA 2020b). The RAC is determined from the active constituent's toxicity to aquatic and sediment dwelling species Table 1. RACs for biocides with use restricted to ships (DCOIT, Thiram) are not included.

In the EU and New Zealand, environmental acceptability is determined by comparing the predicted environmental concentration (PEC), determined using MAMPEC v3.1, to the predicted no-effect concentration (PNEC) (EPA 2013a). The latter is calculated using data from acute and chronic toxicological studies and application of an appropriate "safety" factor determined by consideration of uncertainty in the data (EPA 2013a). According to the risk characterisation process, if the ratio PEC/PNEC, or Risk Quotient (RQ), is less than one, the concentration in the environment is likely to be lower than the critical threshold level and risk is considered acceptable. PNEC values for antifouling biocides were identified in the NZ reassessment of antifouling paints (EPA 2013a, 2013b) and are reproduced in Table 1.
Biocide	RAC	PNEC _{marine}	Unit
Copper present as cuprous oxide	5.2	5.2	µg Cu/L
Copper pyrithione	0.18	0.046	µg ac/L
Copper thiocyanate	2.0	5.2	µg ac/L
DCOIT	-	0.11 ^b	µg ac/L
Dichlofluanid ^a	0.64	0.0265	µg ac/L
Diuron	1.6	0.032	µg ac/L
Thiram	-	1.0	µg ac/L
Zinc pyrithione	1.2	0.046	µg ac/L
Zineb	2.2	0.044	µg ac/L

Table 1 RAC and PNEC for antifouling biocides

Note: **A** Not in any currently approved antifouling products. **b** EPA 2013b. Sources: RACs, APVMA 2020b; PNECs, EPA 2013a.

The NZ EPA commissioned a study to evaluate the OECD Emission Scenario Document, which included running MAMPEC for a range of ports and marinas (Gadd et al. 2011). Predictions were run for 11 ports and 13 marinas in New Zealand, which were compared to the OECD default scenarios. Differences between outcomes for New Zealand locations and the OECD defaults led to a recommendation that New Zealand ports and marinas be used in assessments. The recommended port was Lyttelton, and the recommended marinas Half Moon Bay (marine) and Kinloch (freshwater). The APVMA in Australia accepts MAMPEC modelling using these New Zealand locations to assess the environmental risk of new antifouling products submitted for APVMA approval (APVMA 2020d).

5.3 Discharge modelling

MAMPEC for ballast water, MAMPEC-BW, was developed for the IMO to enable exposure assessment of chemicals in ballast water (van Hattum et al. 2018). The model is used as part of the evaluation methodology for basic and final approval of ballast water treatment systems by the MEPC at the IMO. The emission values for compounds are calculated from the specification of the ballast water discharge rate (in m³/day) and the concentration of the target compound in the discharge (in mg/L). The database includes more than 40 compounds that could be used in ballast water treatment systems. Although antifouling biocides are not included in the MAMPEC-BW database, details of these compounds are in the MAMPEC 3.1 database, and the relevant details can be entered and saved in MAMPEC-BW.

The utility of MAMPEC-BW for assessing contamination from IWC treatment systems has been tested using measurements of treatment system discharge rates and copper concentrations in the effluent from the treatment system in ship trials of the CleanSubSea Envirocart (Appendix B). PECs and RQs were calculated, using Lyttelton Harbour as the example port, and results were also compared to Australian water quality guideline trigger values. For this trial, the calculated PECs were approximately 2 orders of magnitude below the ANZECC / ARMCANZ trigger values.

Using the estimated treatment system discharge volume during a standard working day as an input to MAMPEC-BW, and trial and error, the discharge concentrations that would result in critical PECs were calculated. A copper concentration trigger value for shut down of a clean of 0.5 mg Cu/L was recommended from this work, based the calculation of 0.7 mg Cu/L as the

discharge concentration that would result in the 99% Species Protection Level [SPL], the highest level of protection. This shut down value is specific to the Envirocart system, and would vary on different capture/filtration systems

5.4 Contaminant release from in-water cleaning

5.4.1 Copper

Available information on the copper content and quantity of copper in the biofilm, leached layer, sound paint and paint flakes was reviewed by Morrisey et al. (2013) and, from this, best estimates calculated for use in MAMPEC modelling (Table 2).

Laver	Recreatio	nal vessels		Commerc	ial vessels	Commonte				
Layer	SPC	Ablative	Hard	SPC	Ablative	comments				
Sound paint (μg/cm²/1 μm thickness)	120	120	120	120	120	Fairly certain; data too variable to distinguish between paint types				
Leached layer (µg/cm²/1 µm thickness)	2.4-24	2.4-24	2.4-24	2.4-24	2.4-24	Very uncertain; assumed to be 2-20% of sound paint content				
Biofilm (µg/cm²/event)	50	100	75	25	50	Fairly uncertain				

Table 2 Copper content of different surfaces removed during in-water cleaning

Source: Morrisey et al. 2013, Table 5.2

To estimate the quantity of copper likely to be released during light and aggressive cleaning, available information was used to estimate the depth of leached layer and sound paint that could be removed by the two methods (Morrisey et al. 2013) (Table 3). The entire layer of biofilm was expected to be removed by both methods.

Lavor (um)	Recreatio	nal vessels		Commerc	ial vessels	Comments		
Layer (µm)	SPC	Ablative	Hard	SPC	Ablative	comments		
Leached layer thickness	50	60	75	50	60	Fairly certain		
Light cleaning total removal depth	25	25	25	25	25	Fairly uncertain		
Light cleaning leached layer removal depth	25	25	25	25	25	Fairly uncertain		
Light cleaning sound paint removal depth	0	0	0	0	0	Fairly certain		
Aggressive cleaning total removal depth	75	75	75	75	75	Fairly uncertain		
Aggressive cleaning leached layer removal depth	50	60	75	50	60	Fairly uncertain		
Aggressive cleaning sound paint removal depth	25	15	0	25	15	Fairly uncertain		

Table 3 Layer thickness and removal depth during in-water cleaning

Source: Morrisey et al. 2013, Table 5.3

5.4.2 Other biocides

The same methodology could be applied to antifouling biocides apart from copper, with the proviso that less, if any, data are likely to be available on their concentrations in the biofilm and leached layers. Only the concentration in sound paint could be calculated with reasonable certainty.

5.4.3 In-water cleaning with no waste capture, containment or treatment

The aim of modelling undertaken by Morrisey et al. (2013) was to estimate the copper release from IWC without waste capture, containment or treatment. For this, the release of copper per unit area for the three different coating types and the two cleaning intensities (Table 4), was calculated from copper content of the surface layers (Table 2) and the thickness of layers removed (Table 3Table 3).

Cleaning method and Coating Type	Recreational vessel	Commercial vessel			
Copper release from light cleaning (µg/cm ²)					
SPC	110 - 650	85 - 625			
Ablative	160 - 700	110 - 650			
Hard	135 - 675	N/A			
Copper release from aggressive cleaning (μ g/cm ²)					
SPC	N/A	3145 - 4225			
Ablative	N/A	1994 - 3290			
Hard	N/A N/A				

Table 4 Copper release rates for recreational and commercial vessels

Source: Morrisey et al. 2013, Table 5.5

PECs were determined by MAMPEC modelling for the cleaning of different numbers of recreational and commercial per day, for different sized vessels, for cleaning the full hull, or only the vertical sides or boot-tops, and for two New Zealand marinas (Half Moon Bay, Westhaven) and two harbours (Lyttelton, Auckland). The PECs for total and dissolved copper for the different scenarios were compared to the ANZECC/ARMCANZ (2000) 90% and 95% protection trigger concentrations for copper, and the US EPA (1995) acute criteria for copper.

The conclusions on the copper contamination risks drawn from this study in relation to commercial ships were summarised as follows (Section 5.8; Morrisey et al. 2013):

- Estimated emission rates indicate that uncontained IWC may result in the release of large amounts of total copper. On commercial vessels, this could be up to 68 kg for soft cleaning methods and 300 kg for aggressive cleaning methods. The potential impacts of copper are based on its form (total versus dissolved), and discharges/emissions are rapidly reduced by dilution and binding to dissolved organic carbon. As a result, these estimates may not have the environmental impact that could be expected based on mass alone
- For comparison, the amount of copper passively released from one ship in harbour could be between 0.1 and 1.5 kg per day, depending on the size of the vessel (Table 5.28; Morrisey et al. 2013)

- For IWC of commercial vessels using soft cleaning methods and the upper copper release estimate, most scenarios indicated a low risk based on mixing within the Port of Auckland, but there was a greater likelihood of guideline exceedance within Lyttelton Port, particularly for vessels larger than 100 m. This was attributed to the low flushing associated with this port. The likelihood of exceedance was increased for IWC using aggressive cleaning methods and the upper copper release estimate, and there was a medium or high risk for the majority of aggressive cleaning scenarios within Lyttelton Port
- The number of medium and high-risk scenarios in each port was reduced if the modelling was based on lower copper release estimates. For soft cleaning, all scenarios indicated a low risk in Port of Auckland and, in Lyttelton Port, cleaning more than one vessel of length greater than 200 m per fortnight indicated a medium or high risk. However, for aggressive cleaning, many combinations of vessel numbers and sizes indicated a high risk in both ports
- The volume of copper released in the above scenarios was related to total wetted area of the vessel hull. However, for operational reasons it was considered likely that in-water cleaning carried out as routine maintenance could focus on only a ship's vertical sides or boot-top, as these locations are prone to fouling, and are easily accessible. As expected, the cleaning of only vessel sides or boot-tops reduced the number of medium and high-risk scenarios. For example, all scenarios for aggressively cleaning only boot-tops indicated a low risk in the Port of Auckland and, in Lyttelton Port, only higher cleaning frequencies of larger vessels indicated medium or high risks.

These conclusions could be further summarised to recommend that, without waste capture, aggressive cleaning of entire underwater hulls should not be permitted within ports, particularly those with low flushing rates. However, aggressive cleaning of only boot-tops could be permitted. Light cleaning of entire hulls, to remove only the biofilm and leached layer, could mostly be permitted, except on vessels longer than 100 m in low flushing environments.

For paint flakes, using the calculated copper content of sound paint of $120 \ \mu g \ Cu/cm^2/1 \ \mu m$ of coating thickness, and a dry film coating thickness of $200 \ \mu m$ (2 coats @ $100 \ \mu m$), a flake of 1 cm² would contain 24 mg Cu (Morrisey et al. 2013). Three of these flakes in 1 kg of sediment would raise the sediment copper concentration above the ISQG trigger value in the National Assessment Guidelines for Dredging (CoA 2009). The release of paint flakes during cleaning would therefore be best avoided in harbours and marinas if there is no waste containment.

5.4.4 In-water cleaning with waste capture and containment, but no treatment

With the exception of paint flakes, capture and containment of waste by filtration, with the seawater filtrate discharged without treatment, would not be expected to significantly reduce the concentration of biocide from that in the uptake stream. Both dissolved and some particulate biocides are likely to pass through mesh filtration systems. Biocide associated with slime may be retained on the sieves if associated with macro-biological waste.

Mesh filtration is considered a key step in removing larger paint flakes from the waste stream.

5.4.5 In-water cleaning with waste capture, containment, and treatment

Treatment of the filtrate by cartridge filtration after mesh filtration has been demonstrated to significantly reduce the copper concentration in the waste stream. Reductions of 80% for

dissolved, and 90% for particulate copper, have been measured during trials of the CleanSubSea system that passes the waste stream through high flow microfiltration cartridges after mesh filtration (GRD Franmarine Holdings Ltd, unpublished data).

Various techniques can be used to remove copper from a waste stream, including adsorption, cementation, membrane filtration, electrochemical methods and photocatalysis (Al-Saydeh et al. 2017). The advantages of adsorption using low-cost adsorbents (e.g. zeolites, clay-polymer composites, modified biopolymers) are the low initial cost and simple design which makes them suited to IWC treatment systems. More than 95% of copper can be removed (Chouyyok et al. 2010, Khulbe & Matsuura 2018). Organo-clay absorption has been proposed for post-filtration treatment of IWC waste streams in California (California Water Boards 2013). Membrane filtration systems are compact, so also suitable, but have the disadvantage of high operating costs (Al-Saydeh et al. 2017).

MAMPEC-BW modelling has shown that PECs can be calculated from measurements taken during in-water cleaning trials with waste capture, containment and treatment, and that these are well below environmental guidelines (Appendix B).

6 Coating suitability & acceptability for in-water cleaning

6.1 Coating

6.1.1 Coating type

1) Biocidal

In-water cleaning of biocidal coatings will result in the removal of biocide along with biofouling growth, with the amount of biocide released likely to depend on the method of cleaning, the aggressiveness of the clean, the type of coating, the age of the coating, and the use and methods of waste treatment. The risk of this contaminant posing a risk to the marine environment depends both on the quantity of biocide discharged, and the physical and hydrodynamic characteristics of the receiving environment, i.e. the volume of a harbour and water exchange rate.

The modelling of Morrisey et al. (2013) estimated contamination levels for multiple scenarios combining vessel sizes, coating types, cleaning frequencies and cleaning aggressiveness, with no capture or treatment of waste. This research concluded that under some scenarios, cleaning of biocidal coatings without capture could be undertaken without the biocide release exceeding environmental guidelines. The acceptable scenarios were those of light cleaning that removed only the biofilm and leached layer and, to limit any need for aggressive cleaning, if needed, to the boot top. Hull grooming is considered to equate to light cleaning and to not pose an unacceptable contamination risk.

The chemical contamination risks associated with cleaning biocidal coatings can be further minimised by treating water entrained in the waste capture and containment system before discharge. This can reduce the quantity and concentration of the biocide in the discharge to acceptable levels (Appendix B).

A pre-requisite to in-water cleaning needs to be the ship holding a valid AFS Certificate to verify that the coating is compliant with the AFS Convention (IMO 2005). As it is now 17 years since the application of organotin antifouling paints was banned, and at least 12 years since sealing of old organotin coatings was permitted, the presence of organotin coatings is highly unlikely though possible, particularly in parts of the world where organotin coatings are still available. For example, one US paint company continues to advertise tributyltin-containing antifouling paints as "Export – (Non-US)" (Sea Hawk 2020). However, if a ship was built before 2003, the Record of AFS required by the Convention should be inspected to ensure that organotin coatings are not retained beneath a barrier coat. Most vessels of this age are likely to have had the hull fully blasted and a completely new underwater hull coating system applied during the past 12 years.

2) Non-biocidal

Although free of biocides, in-water cleaning has the potential to damage silicone FR coatings due to their susceptibility to abrasion damage. The coatings should only be cleaned by non-contact or contact methods approved by the coating manufacturer. Water-jetting applied at the appropriate pressure by skilled operators should not damage these coatings.

Mechanically resistant coatings are not considered to pose any chemical contamination risk from in-water cleaning, irrespective of method.

6.1.2 Biocide type

Cuprous oxide continues as the most effective and most commonly used antifouling biocide and environmental effects are ameliorated by the reduction in bioavailability and toxicity almost immediately after release (Brooks & Waldock 2009). Copper is, however, a contaminant of concern and subject to environmental regulation (e.g. ANZECC/ARMCANZ 2000). Management of copper releases to meet environmental regulations can be achieved by controls on the type of cleaning undertaken and/or the use of treatment systems.

The newer generation of antifouling booster biocides (e.g. DCOIT, zinc pyrithione, copper pyrithione) have passed stringent regulatory reviews prior to approval, which included assessment of toxicology, degradation, and environmental fate (e.g., NRA 2001, APVMA 2005). The cleaning of coatings containing these biocides is likely to be acceptable with similar constraints to those for copper-based coatings. However, MAMPEC-BW modelling is needed to ensure this is the case.

A number of older biocides grandfathered into the Australian registration system, or used in coatings applied overseas, have been banned or banning has been proposed by other countries because of environmental or human health concerns (e.g., EPA 2013c). These include diuron, cybutryne, ziram and chlorathonil. The release of these biocides into the environment during inwater cleaning conducted without waste capture and full containment could pose an unacceptable risk and would seem best avoided. Should there be a critical need to clean a coating containing these biocides, wastewater treatment and containment should be subject to detailed review and the disposal of the liquid waste at an approved waste facility possibly considered. The review should consider, at least, the demonstrated capacity of the treatment system to ensure any discharges are within an acceptable level if there is one, and the condition of the paint system.

6.1.3 Coating age

When applied, the antifouling system is, or should be, specified for the planned service interval to the next dry-docking. Common service intervals are 24, 36, 60 and 90 months. The effective service life is achieved by the choice of antifouling coating and the thickness of coating applied and presumes a specified level of operational activity. The reliability of coatings in ensuring effective biofouling control through the required service interval varies with the type of coating (and often cost) (Thomason 2010).

The service life and reliability of insoluble matrix coatings are generally less than soluble matrix/ablative coatings which, in turn, are generally less than SPC coatings (Almeida et al. 2007, Lewis 2010). If the antifouling is close to or has exceeded its specified service life, the presence of substantial macrofouling would be indicative of biocide depletion that warrants renewal of the system in dry-dock. IWC of a system near, at or over the specified service life should not be a means to postpone or delay a dry-docking, as the coating is likely to rapidly refoul (as per Guidelines).

If a ship has not operated as planned, for example by having an unexpected, extended lay-up, macrofouling may establish as a consequence of the ablation or polishing rate not enabling the

critical biocide release rate. Coatings can also fail due to the formation of insoluble compounds on the coating surface, for example basic cupric carbonate (Ferry & Ketchum 1952) or, if the vessel has operated in highly sulphurous water, copper sulphide (Edyvean & Silk 1988). In these circumstances, proactive IWC may rejuvenate and reactivate the coating through removal of the biofilm, other surface deposits, and the leached layer.

6.1.4 Coating condition

The condition of a coating can deteriorate within the planned service life as a consequence of poor surface preparation, poor paint application, environmental conditions at the time of application, incompatibility of coatings, defective product, or in-service damage. The consequence can be delamination, lifting or blistering of the paint system that generates paint flakes. If the failure is at the hull plate/coating interface, cathodic protection systems and reactions can cause additional delamination radiating out from the initial point of failure (Fitzsimons 2011). Should this damage be extensive, the ship would need to dry-dock for coating system repair.

Fortunately, major failures of the full underwater coating systems are less common now than in the past, due to the high-performance anticorrosive coatings in use. Inter-coat failures under or between antifouling coatings can still occur because of surface contamination at the time of application (Fitzsimons 2011).

In any IWC operation, the generation and release to the environment of paint flakes should be avoided. If flaking is extensive, or potentially extensive during the clean, then consideration should be given to either not proceeding with the clean, or to ensure capture and containment of dislodged flakes by mesh filtration.

6.2 Biofouling

6.2.1 Biofouling type

The presence of a biofilm on an antifouling coating is almost assured, although the composition, extent and thickness can vary with the type of antifouling, the biocide or biocides, age of the coating, and the location on the hull (e.g. highly lit vessel sides or flat bottom). Removal of biofilms by in-water hull grooming or cleaning is not considered to pose an unacceptable chemical contamination risk (Morrisey et al. 2013).

As discussed in Section 3.2 the presence of secondary biofouling is an indication that the biocide release has dropped below the critical level. The primary macroscopic colonisers are frequently highly copper tolerant species that have been selected and spread globally on ships since copper-based antifouling coatings were first applied (Iron and Steel Institute 1944, Ayers & Turner 1952, Wood & Allen 1958, Lewis 2002). Foremost among these are the filamentous green algae (*Ulva* spp.) and the encrusting bryozoan *Watersipora*, followed by calcareous tubeworms (*Hydroides* spp.) and some acorn barnacles (e.g. *Amphibalanus amphitrite*) (Wisely 1958, Callow 1990, Blossom et al. 2016). If these species are the only organisms present across a hull surface, and the hull is more than several months within its service life, then in-water cleaning may rejuvenate the coating and improve hull efficiency.

6.2.2 Biofouling level

Various systems to quantify the level and extent of biofouling over a hull have been developed (Table 5, Table 6). These do not consider the level of biofouling in niches, such as on dock block

marks, around thrusters and propulsion units, inside sea chests etc., where localised aggregations of growth may establish.

In regard to in-water cleaning, the US Navy recommended that ships should be inspected regularly to determine if cleaning is necessary (NSSC 2006). Advice is given that "delaying full hull cleaning to the point where a significant amount of hard fouling has formed (FR-50 and above for non-ablative anti-fouling paints; FR-40 for ablative and self-polishing paints) can result in damage to the paint system". A corresponding LOF recommendation would be to not clean if the LOF is 4 or above. Removal of fouling at this rating would be considered as reactive, not proactive cleaning.

Table 5	Level	of	Fouling	(LOF)
---------	-------	----	---------	-------

Level of Fouling	Description
LOF < 2	clean hull or slime layer
LOF 2	1-5% cover of macrofouling
LOF 3	6-15% cover of macrofouling, patchy with only one or several taxa
LOF 4	16-40%, extensive fouling, with abundant assemblages of multiple taxa
LOF 5	41-100%, very heavy fouling, with diverse assemblages covering most of the hull

Source: Floerl et al. 2005

Table 6 Fouling Ratings Scale

Туре	Fouling rating (fr)	Description
Soft	0	A clean, foul-free surface; red and/or black AF paint or bare metal surface.
Soft	10	Light shades of red and green (incipient slime). Bare metal and painted surfaces are visible beneath the fouling.
Soft	20	Slime as dark green patches with yellow or brown colored areas (advanced slime). Bare metal and painted surfaces may be obscured by the fouling.
Soft	30	Grass filaments up to 3 inches (76 mm) in length, projections up to $\frac{1}{4}$ inch (6.4 mm) in height; or flat network of filaments, green, yellow, or brown in color, or soft non calcareous fouling such as sea cucumbers, sea grapes, or sea squirts projecting up to $\frac{1}{4}$ inch (6.4 mm) in height. The fouling cannot be easily wiped off by hand.
Hard	40	Calcareous fouling in the form of tube worms less than ¼ inch (6.4 mm) in diameter or height.
Hard	50	Calcareous fouling in the form of barnacles, less than $\frac{1}{4}$ inch (6.4 mm) in diameter or height.
Hard	60	Combination of tubeworms and barnacles less than ¼ inch (6.4mm) in diameter or height.
Hard	70	Combination of tubeworms and barnacles greater than ¼ inch (6.4 mm) in diameter or height.
Hard	80	Tubeworms closely packed together and growing upright away from surface. Barnacles growing one on top of another, ¼ inch (6.4 mm) or less in height. Calcareous shells appear clean or white in color.

Туре	Fouling rating (fr)	Description
Hard	90	Dense growth of tubeworms with barnacles, ¼ inch (6.4 mm) or greater in height. Calcareous shells brown in color (oysters and mussels); or with slime or grass overlay.
Composite	100	All forms of fouling present, soft and hard, particularly soft sedentary animals without calcareous covering (tunicates) growing over various forms of hard growth.

Source: NSSC 2006

7 Recommendations on IWC with respect to contamination

7.1 What to clean

The removal of biofouling from the underwater hull and niches of a vessel is undertaken for two reasons: to restore or improve operational performance and/or to manage the risk of transferring invasive marine species (IMS). For the former, the priority is to remove biofouling from hull surfaces to reduce hull friction, propellers to restore propulsion efficiency, and from niches where the marine growth obstructs performance, such as on seawater intakes and hull sensors. For the latter, although a clean hull is important, more often the aggregations of biofouling in protected niches such as sea chests and thruster tunnels, under anodes and rope guards, along bilge keels, etc., are of greater concern (Davidson et al. 2016).

7.2 When to clean

7.2.1 Hull grooming and proactive cleaning

Hull grooming and proactive cleaning are regular cleaning to remove early stage biofouling, the biofilm (primary biofouling / slime) and newly settled macrofouling, and, if performed regularly, propeller polishing. The optimum frequency for this cleaning has not been clearly established, and would vary with the coating type, the operational profile of the vessel, and the operational environment. A general recommendation is the more often the better. For commercial trading vessel, to maximise efficiency, a more specific suggestion is at least twice a year. The earlier the cleaning is completed in the process of biofouling development, the less likely will be the requirement for biological waste capture.

IWC of dock block marks immediately after a vessel has left dry-dock is also considered a proactive measure to reduce the likelihood of new biofouling settlement and development on the biofouling residues unable to be removed in the dry-dock because of block positions.

Proactive cleaning is also consistent with the 'clean before you leave' biofouling management strategy to minimise the risk of IMS translocation (DoA/NZMPI 2015, Georgiades et al. 2018).

7.2.2 Reactive cleaning

Reactive cleaning is cleaning to remove established macrofouling to restore hull efficiency and other operational functions, or to reduce IMS translocation risk. For the former, the recommendation is that cleaning should be undertaken when the level of fouling is no greater than LOF 3 (Morrisey et al. 2013), or a fouling rating of no more than FR 40. For the latter, the general recommendation is 'clean before you leave', but the more common practice is currently 'clean when I have to' to meet requirements or regulations in the destination port.

7.3 When not to clean

7.3.1 AFS age

IWC should not be undertaken to remove established, extensive and well-developed biofouling that has resulted from antifouling coating failure, or the system being close to, at, or beyond the service life specified at the time of application (Guidelines). Substantial biofouling, or near-end

of service life are indicators that the AFS has failed or is depleted, and rapid refouling is both likely and possibly enhanced by further degradation of the coating by IWC. For these circumstances, the vessel needs to be dry-docked for AFS replacement or renewal. IWC should not be undertaken to delay or postpone dry-docking beyond the planned date. If evidence cannot be provided for specification of a longer service life, then the default time should be 24 months.

The exception would be if the biofouling is a confirmed biosecurity risk to the present or forward locations.

7.3.2 AFS formulation

IWC should not be undertaken on any vessel that may have organotin-based coatings. Their absence should be verified by inspection and confirmation of validity of the vessel's AFS certificate. If a vessel was built before 2003, the Record of AFS should be examined to ensure no organotin coating remains sealed under a barrier coat.

It is recommended that IWC not be undertaken if the AFS contains any of the biocides cybutryne, diuron, chlorothalonil, and ziram, which have been banned, or are to be banned overseas. The Record of AFS identifies all biocides present in the vessel's AFS. Should cleaning of such coatings be imperative for emergency reasons, consideration should be given to undertaking the IWC in offshore waters, with due attention to OH&S risks, or capturing all liquid waste for disposal at an appropriate waste facility.

7.4 How to prepare for IWC

To prepare for cleaning, details of the AFS need to be confirmed, and a hull survey undertaken to determine the biofouling type, abundance and distribution, and the condition of the underwater coating system. If only hull grooming is proposed, the survey could be by diver or ROV; for hull cleaning, a dive inspection is recommended.

If contaminants will be discharged during the IWC, characteristics of the receiving water body should be understood to ensure contaminant discharges do not lead to exceedance of environmental protection standards. MAMPEC v3.1 or MAMPEC-BW modelling may assist by enabling PEC estimation.

7.5 Risk assessment of the IWC

If surfaces coated with biocidal AFC are to be cleaned, a two-stage risk assessment is proposed to determine whether the chemical discharge from the clean is environmentally acceptable. The method proposed for this assessment is calculation of PECs using MAMPEC v3.1 and MAMPEC-BW.

7.5.1 Stage 1 Risk Assessment: pre-emptive acceptability of hull grooming

To determine if containment and treatment of the dislodged waste is needed for hull grooming in a particular location, MAMPEC v3.1 should be used to determine the limit, in terms of vessel size and/or number of vessels/day, of grooming that can be undertaken in that location without resulting in environmental harm. For this, Morrisey et al. (2013) applied the following inputs:

• For the range of vessels visiting the location, lengths and corresponding underwater surface area of the vessels

- Specification of soft cleaning only (slime + leached layer)
- Marina / harbour parameters (use Lyttelton Port as the default harbour, and Half Moon Bay as the default marina, if parameters for the actual location for the IWC are not known)
- Best available estimates of the biocide content of the leached layer and slime should be used, with the values applied in Morrisey et al. (2013) used as defaults.

The acceptable outcome to allow grooming to proceed without capture, containment and treatment of wastewater in a location is those vessel sizes or numbers of vessels per day that return a "low risk" outcome, defined as an average PEC below the ANZECC 90% protection guideline (Morrisey et al. 2013) or a PEC/PNEC ratio <1.

7.5.2 Stage 2 Risk Assessment: IWC acceptability

If the proposed grooming is not within the acceptance limits determined by the Stage 1 Risk Assessment (e.g. the vessels is larger than those accepted or cleaning frequency is exceeded), or if IWC is proposed to remove secondary biofouling in addition to slime, and capture, containment and treatment of the wastewater is required with treated water to be discharged back into the local environment, then the acceptability of the discharge should be assessed using MAMPEC-BW with the following inputs:

- Marina / harbour parameters (use Lyttelton Port as the default harbour, and Half Moon Bay as the default marina, if parameters for the actual location for the IWC are not known)
- Data for biocides present in the AFC (if a biocide is not in the MAMPEC-BW database, data can be found in the MAMPEC v3.1 database)
- Contaminant concentration in the treated discharge and volume of waste to be discharged per day that are specific to the treatment system, and verified in trials of that system

The outcome to allow IWC to proceed without additional management (e.g. operational time limits, additional water treatment, disposal of liquid waste to an approved facility etc.) is also proposed as meeting the "low risk" criterion as defined above (section 7.5.1).

7.6 How to clean

IWC should be restricted to areas where growth is of concern, be it on planar surfaces that impacts on ship efficiency, exceeds acceptable levels required by ports, states or other regulatory authorities for entry into waters within their jurisdiction, or both. The least aggressive and most appropriate methods should be used to achieve the required result, and the cleaning method should be chosen to ensure the coating is not damaged. For example, manual cleaning may be preferable to machine cleaning if biofouling is scattered across the hull or in localised aggregations, or water jetting preferable to stiff-bristled brush carts if only slime or early stage secondary biofouling is to be removed. A combination of methods is likely to be required for the outcome of a 'clean hull'.

7.7 When to contain the waste

With regard to chemical contamination, IWC waste should be captured and contained if the coating system is defective and paint flakes are likely to be removed during cleaning. Mesh filtration at 50 μ m or less, as recommended in the current IWC guidelines to ensure minimal release of biological material, would also remove flakes from the waste stream.

7.8 When to treat the waste

Waste should be treated if the IWC is to be conducted in a semi-enclosed inshore environment and all, or sections of the hull plate on the vertical sides and/or flat bottom are to be cleaned. Exceptions are if:

- the coating is a non-biocidal coating
- IWC will be by manual methods only, or restricted to niche areas
- the outcome of MAMPEC v3.1 modelling for the IWC is "low risk"
- the IWC is undertaken in open waters.

7.9 In summary

To ensure IWC (including grooming) does not result in potentially harmful chemical contamination of local waters, IWC should:

- be restricted to areas on wetted surfaces where growth is unacceptable, and the least aggressive and most appropriate methods used to achieve the required result. The cleaning method should be chosen to ensure the coating is not damaged. A combination of methods is likely to be required for the outcome of a 'clean hull', which includes all wetted surfaces
- capture and contain paint waste if the coating system is defective and paint flakes are likely to be removed during cleaning
- be monitored to ensure the cleaning method is not damaging the coating system
- if the IWC is to be conducted in a semi-enclosed, shallow inshore environment, and/or in close proximity to sensitive areas/threatened species per EPBC Act and all, or sections of the hull plate on the vertical sides and/or flat bottom are to be groomed or cleaned, be subject to pre-emptive risk assessment to determine
 - firstly, acceptability of hull grooming without waste capture and treatment for vessels up to a specified size and frequency in specified locations
 - secondly, acceptability of capture, containment and treatment systems to ensure the low risk of discharges from IWC or hull grooming not acceptable under the previous point

The current guidelines for Anti-Fouling and In-Water Cleaning (DoA/NZMPI 2015) includes a decision-support tool for in-water cleaning. To show how decisions on options for capture, containment and treatment to address potential chemical contamination could be included in this tool, additional steps have been included in a modified flow chart (Figure 1). Three outcomes are possible:

- 1) In-water cleaning acceptable without requirement to contain cleaning waste, provided conditions A and B are met and a non-abrasive cleaning method is used to avoid contaminant risk and coating damage
- 2) In-water cleaning acceptable
- 3) In-water cleaning not recommended. Dry-docking recommended for cleaning and antifouling renewal.

IWC should not:

- damage the coating
- cut deeply in to sound paint below the leached layer
- be performed in shallow, enclosed water bodies without a risk assessment
- be permitted if the vessel does not have a valid International Anti-Fouling System Certificate or Declaration on Anti-Fouling System that lists biocides present in the coating
- be permitted if the AFC contains diuron, cybutryne, ziram, chlorothalonil or other biocides restricted or banned elsewhere in the world
- be permitted if the specified service-life for the antifouling systems applied at the last drydocking has been exceeded and is not recommended if the end of the service life and scheduled dry-docking is within 6 months
- be undertaken if there is extensive significant coating system breakdown with flaking or lifting of the paint. The vessel should, instead, be dry-docked for coating system repair, renewal or replacement
- be undertaken without capture if there are areas of significant breakdown and cleaning is required for emergency reasons, such as biosecurity emergencies.

To refine and improve outcomes of the above recommendations on risk assessment, additional data of benefit would include:

- physical and hydrological parameters for harbours and other water bodies where IWC could be undertaken to define those locations in MAMPEC modelling
- the biocide content of the leached layer and biofilm that develops on the surface of AFCs, including on different AFCs and AFCs of different ages.

Figure 1 Decision-support tool for in-water cleaning, with decision points added to address potential chemical contamination



Appendix A: APVMA approved antifouling products

Table A1 APVMA approved antifouling products, 2020-03

Company / Product	Approval No.	Year of 1st Approval	Cuprous oxide	Cuprous thiocyanate	Diuron	Thiram	Zineb	DCOIT	Zinc pyrithione	Copper pyrithione
AKZO NOBEL PTY LIMITED										
Interclene 165 Bright Red Tin Free Antifouling	45412	1995	+	-	+	-	-	-	-	-
International VC Offshore Racing Antifouling	49609	1997	+	-	+	-	-	-	-	-
Intersmooth 360 SPC Antifouling	51971	2002	+	-	-	-	-	-	+	-
International Awlcraft Antifouling	58268	2004	+	-	+	-	-	-	-	-
International Biolux New Technology Trilux 33 Hard Antifouling for Aluminium	58567	2006	-	+	-	-	-	-	+	-
Intersmooth 7460HS SPC Antifouling	65261	2014	+	-	-	-	-	-	-	+
International Biolux New Technology Micron Extra 2 High Strength Self Polishing Antifouling	80681	2016	+	-	-	-	+	-	-	-
International Micron 77 Biolux SPC True SPC Antifouling	80827	2017	+	-	-	-	-	-	-	+
Interspeed 376 Hard Antifouling for Aluminium	81819	2017	-	+	-	-	-	-	+	-
International VC Offshore Hard Racing Antifouling	81981	2017	+	-	-	-	-	-	-	-
Interswift 6800HS Tin Free SPC Antifouling	82066	2017	+	-	-	-	+	-	-	-
International Biolux New Technology Ultra 2 High Strength Hard Antifouling	83417	2018	+	-	-	-	+	-	-	-
International Biolux New Technology Micron AP High Strength Self Polishing Antifouling	83562	2018	+	-	-	-	+	-	-	-
International Micron 350 Premium Self Polishing Antifouling	86008	2019	+	-	-	-	-	-	-	-

Company / Product	Approval No.	Year of 1 st Approval	Cuprous oxide	Cuprous thiocyanate	Diuron	Thiram	Zineb	DCOIT	Zinc pyrithione	Copper pyrithione
International Micron 99 Biolux SPC Premium Self Polishing Antifouling	85986	2019	+	-	-	-	-	-	-	+
Intercept 8500 Tin Free Linear Polishing Polymer Antifouling	86812	2019	+	-	-	-	-	-	-	+
CHUGOKU MARINE PAINTS LTD										
Seajet 039 Platinum 2-Components Antifouling	87337	2020	+	-	-	-	-	-	+	-
HEMPEL (AUSTRALIA) PTY LTD										
Hempels Antifouling Mille Dynamic ALU	46918	1995	-	+	+	-	-	-	-	-
Hempel's Antifouling Globic	54514	2002	+	-	-	-	-	+	-	-
Hempel's Antifouling Olympic 86951	61966	2008	+	-	-	-	-	-	-	-
Hempel's Antifouling Olympic 86901	61970	2008	+	-	-	-	-	-	-	-
Hempaguard X7 89900 Fouling Defence Coating	83065	2017	-	-	-	-	-	-	-	+
Hempel's Antifouling Globic 9000 78950	83857	2018	+	-	-	-	-	-	-	+
Hempel's Antifouling Globic 9000 78900	85125	2018	+	-	-	-	-	-	-	+
Hempel's Antifouling Alu Xtra NCT 74770	86772	2019	-	+	-	-	-	-	+	-
JOTUN AUSTRALIA PTY LTD										
Antifouling Seaguardian	40163	1995	+	-	-	-	-	-	-	-
Antifouling Super Tropic	40164	1995	+	-	-	-	-	-	-	-
Antifouling Seasafe	46487	1997	-	+	-	-	+	-	-	-
Antifouling Seavictor 50	45488	2000	+	-	-	-	-	+	-	-
Antifouling Seavictor 40	46489	1995	+	-	-	-	-	-	-	-

Company / Product	Approval No.	Year of 1st Approval	Cuprous oxide	Cuprous thiocyanate	Diuron	Thiram	Zineb	DCOIT	Zinc pyrithione	Copper pyrithione
Antifouling Seaquantum Ultra S	64505	2012	+	-	-	-	-	-	-	+
Antifouling Seasafe Ultra	65433	2012	-	+	-	-	-	+	-	-
Antifouling SeaForce Active Plus	87840	2020	+	-	-	-	+	-	-	+
MARLIN S.R. L Velox Plus Antifouling	66047	2013	-	-	-	-	-	-	+	-
NEW NAUTICAL COATINGS, INC. Sea Hawk Yacht Finishes Premium Quality Biocop TF Antifouling Coating	64185	2011	+	-	-	-	-	-	+	-
Sea Hawk Premium Yacht Finishes Premium Quality AF33 Eroding Antifouling	69531	2015	+	-	-	-	-	-	-	-
Sea Hawk Premium Yacht Finishes Premium Quality CuKote Eroding Antifouling	69582	2015	+	-	-	-	-	-	-	-
NORGLASS LABORATORIES PTY LTD Norglass Topflight Antifouling	54048	2001	+	-	-	-	-	-	-	-
PPG INDUSTRIES AUSTRALIA PTY LTD										
ABC 3 Antifouling	55875	2002	+	-	-	+	-	-	-	-
Ecofleet 290 Antifouling	63486	2010	+	-	+	-	-	-	-	-
Ecofleet Alloy Antifouling	64189	2009	-	+	+	-	-	-	-	-
RESENE PAINTS (AUSTRALIA) LIMITED Altex Coatings Industrial & Marine AF3000 Anti-Fouling	56644	2003	+	-	-	+	-	-	-	-
Altex Yacht & Boat Paint No 5 Antifouling	58058	2003	+	-	-	+	-	-	-	-
Altex Yacht & Boat Paint No 5 Antifouling Oyster White	58059	2004	+	-	-	+	-	-	-	-

Company / Product		Approval No.	Year of 1st Approval	Cuprous oxide	Cuprous thiocyanate	Diuron	Thiram	Zineb	DCOIT	Zinc pyrithione	Copper pyrithione
Carboline Sea-Barrier 1000 Antifouling		64129	2010	+	-	-	+	-	-	-	-
Carboline Sea-Barrier 3000 Antifouling		64133	2009	+	-	-	+	-	-	-	-
Petit Marine Paint Vivid Antifouling Paint / Carboline Sea Barrier Alloy 100 AU		66263	2015	-	+	-	-	-	-	+	-
Altex Yacht & Boat Paint No. 5 Plus Antifouling		86349	2018	+	-	-	+	-	-	-	-
TOPLINE PAINT PROPRIETARY LIMITED											
Marine Systems Traditional Copper Based Antifouling		48965	1996	+	-	-	-	-	-	-	-
VALSPAR PAINT (AUSTRALIA) PTY LTD											
Wattyl Protective and Marine Coatings Seapro Cu120 Antifouling		52242	2000	+	-	+	-	-	-	-	-
Wattyl Protective and Marine Coatings Seapro Plus 100 Antifouling		62940	2008	-	+	+	-	-	-	-	-
WAGON PAINTS AUSTRALIA PTY LTD											
Transocean Optima Antifouling 2.32		84506	2018	+	-	-	-	-	-	-	-
	TOTALS	52		41	9	8	7	6	3	9	10

Source: Australian Pesticides and Veterinary Medicines Authority

Appendix B: Risk assessment of chemical discharge from in-water cleaning

Application of MAMPEC Modelling

Included with permission of CleanSubSea, Henderson, WA



RISK ASSESSMENT OF CHEMICAL DISCHARGE FROM IN-WATER CLEANING APPLICATION OF MAMPEC MODELLING

Report to CleanSubSea, Henderson, WA

John A Lewis, ES Link Services Pty Ltd

January 2020

In-water cleaning of vessels to remove biofouling is increasingly promoted as a tool to minimise the environmental impact of shipping by reducing hull friction which, in turn, reduces fuel consumption and consequent greenhouse gas emissions, and to minimise the risk of translocating potentially invasive marine species. However, in-water cleaning is considered to itself pose an environmental risk by the release and potential accumulation in the environment of chemical contaminants from the vessel's hull coating(s), and the release of non-indigenous species (as adults, larvae or viable propagules) into new environments¹. The latter concerns have led to restriction or banning of in-water cleaning by some jurisdictions.

To address the environmental risks posed by in-water cleaning, the Australian and New Zealand Governments developed guidelines on best practice for the management of biofouling that included the intention of assisting authorities with decisions on the appropriateness of in-water cleaning operations in general, and on a case-by-case basis². The guidelines include "recommendations for decision making on in-water cleaning" and a decision support tool to aid decision making on in-water cleaning based on these recommendations. The emphasis of these recommendations was on the perceived biosecurity risk of biofouling with different requirements for biological waste containment assigned to biofouling of regional, domestic and international origin. For contaminant discharges, the recommendation made was that "contaminant discharges must meet any local standards or requirements".

Ensuring that contaminant discharges from in-water cleaning are acceptable has proven to be difficult due to the absence of any clear standards or limits for contamination concentrations in discharges. Comparisons have been drawn with trigger values in the ANZECC/ARMCANZ Water Quality Guidelines³, which were calculated at four different species protection levels, 80%, 90%, 95% and 99%, that signify the percentage of species expected to be protected. However, these trigger values were developed with respect to concentrations in the environment, not in discharges or other inputs into the environment. Dilution of a discharge on release into a receiving water

¹ Morrisey et al. 2013. In-water cleaning of vessels: Biosecurity and chemical contamination risks. MPI Technical Paper No: 2013/11. New Zealand Government Ministry of Primary Industries, Wellington, New Zealand.

² Department of the Environment and New Zealand Ministry of Primary Industries. 2015. Anti-fouling and inwater cleaning guidelines. Department of Agriculture, Canberra, ACT.

³ [Section] 3.4 Water quality guidelines for toxicants. In, ANZECC & ARMCANZ (2000). *Australian and New Zealand Guidelines for Fresh and Marine Water Quality*. Australian and New Zealand Environment and Conservation Council & Agriculture and Resource Management Council of Australia and New Zealand.

body would lower the contribution of the contaminant to the environmental concentration with the extent dependent on the volumes of both the discharge and the receiving environment.

The following discussion proposes a method to determine the acceptability of chemical contaminant discharges from in-water cleaning treatment systems.

MAMPEC

MAMPEC (Marine Antifouling Model to Predict Environmental Concentrations) is an integrated hydrodynamic and chemical fate model, originally developed to predict environmental concentrations for the exposure assessment of antifouling substances⁴. The model, adopted by the OECD, predicts concentrations of antifouling biocides in generalised "typical" marine environments, including harbours, marinas and the open sea, from the input of emission factors (e.g., biocide leaching rates, shipping intensities, residence times, ship hull underwater surface areas), compound-related properties and processes, and hydrodynamics related to the specific environment. The model has been validated for a number of compounds and has been recognised by regulatory authorities in the EU, other OECD countries, the USA, Japan, New Zealand and Australia. In Australia, the Australian Pesticides and Veterinary Medicines Authority (APVMA) accepts MAMPEC modelling for the environmental risk assessment of new antifouling products submitted for approval. Default values for 10 common antifouling biocides are included in the database.

A special version of MAMPEC for ballast water, MAMPEC-BW, was developed for the International Maritime Organization (IMO) to enable exposure assessment of chemicals in ballast water⁵. The model is used as part of the evaluation methodology for basic and final approval of ballast water treatment systems by the Marine Environment Protection Committee (MEPC) of IMO. The emission values for compounds are calculated from the specification of the ballast water discharge rate (in m³/day) and the concentration of the target compound in the discharge (in mg/L). The database includes more than 40 compounds.

For antifouling coatings, environmental acceptability is determined by comparing the predicted environmental concentration (PEC), determined using MAMPEC, to the predicted no-effect concentration (PNEC). The latter is calculated using data from acute and chronic toxicological studies and application of an appropriate "safety" factor determined by consideration of uncertainty in the data⁶. According to the risk characterisation process, if the ratio PEC/PNEC, or Risk Quotient (RQ), is less than unity, the concentration in the environment is likely to be lower than the critical threshold level and risk is considered low.

⁴ van Hattum et al. 2016. MAMPEC 3.1 Handbook. Deltares, The Netherlands.

⁵ van Hattum et al. 2018. User Manual – Quick Guide. MAMPEC 3.1 / MAMPEC-BW 3.1. Version 3.1.0.5. Deltares, The Netherlands.

⁶ Senda, T. 2009. International trends in regulatory aspects. In, Arai et al., *Ecotoxicology of Antifouling Biocides*. Springer.

The New Zealand Environmental Protection Authority (NZ EPA) adopted the RQ methodology to characterise the environmental risk of biocides contained in antifouling paints, as adopted by the European Union⁷. For copper, the PNEC_{marine} value adopted by the NZ EPA in this report was 2.6 μ g/L.

The PEC can also be compared to water quality guidelines, as in the Morrisey et al. report¹. In this report, low risk was defined as average PEC below the ANZECC 90% protection guideline, medium risk as average PEC above the ANZECC 90% protection guideline but below the USEPA acute criteria, and high risk as average PEC above the USEPA acute criteria.

In New Zealand, the NZ EPA commissioned a study to evaluate the OECD Emission Scenario Document, which included running MAMPEC for a range of ports and marinas⁸. Predictions were run for 11 ports and 13 marinas in New Zealand, which were compared to OECD default scenarios. Differences between outcomes for New Zealand locations and the OECD defaults led to a recommendation that New Zealand ports and marinas be used in assessments. The recommended port was Lyttelton, and the recommended marinas Half Moon Bay (marine) and Kinloch (freshwater). The APVMA in Australia accepts MAMPEC modelling using these New Zealand locations to assess the environmental risk of new antifouling products submitted for APVMA approval.

MAMPEC Modelling of In-Water Cleaning System Discharges

Measurements undertaken during trials of the CleanSubSea Envirocart system provide data suitable as inputs for MAMPEC modelling.

Daily discharge volume

In recent cleans undertaken on RAN frigates the average discharge volume of treated wastewater was 69.33 m³/hour and average operation time through a working day was 5.56 hours. Using 70 m³/h for 6.0 h/day, a base value for daily discharge is 420 m³/day.

Contaminant concentration

The following copper concentrations have been measured in treated effluent samples during Envirocart trials:

⁷ Preliminary Risk Assessment: Antifouling paints reassessment. June 2012. Environmental Protection Authority, New Zealand Government.

⁸ Gadd, J., Depree, C., Hickey, C. 2011. Relevance to New Zealand of the OECD Emission Scenario Document for Antifouling Products: Phase 2 Report. NIWA Client Report HAM 2011-005. National Institute of Water & Atmospheric Research Ltd, Hamilton, NZ.

Vessel	Date	Location	mg Cu/L		
			Min	Max	Mean <u>+</u> SD
Svitzer Falcon	2015 ⁹	Fremantle, WA	0.012	0.037	0.019 <u>+</u> 0.0096
HMAS Warramunga	2019 ¹⁰	Sydney, NSW	0.018	0.05	0.031 <u>+</u> 0.0097
HMAS Arunta	2019	Garden I., WA	0.009	0.19	0.054 <u>+</u> 0.0677

From these results, a base value of 0.05 mg Cu/L is proposed for MAMPEC calculations.

MAMPEC calculations

Using an emission discharge of 420 m³/day and a copper concentration of 0.05 mg Cu/L, which results in a total emission of 21 g Cu/d, and the environmental parameters for Lyttleton Harbour, the following PECs were calculated using the MAMPEC-BW model:

<u>Harbour</u>

	μg Cu /L		
	Total conc.	Freely dissolved	
Maximum conc.	0.0398	0.0263	
95% conc.	0.0398	0.0263	
Average conc.	0.0214	0.0141	
Minimum conc.	0.0029	0.0019	

⁹ Lewis JA (2016), Envirocart Trial – October 2015: 1. Environmental Discharge. Report prepared for GRD-Franmarine Holdings Ltd. ES Link Services Pty Ltd.

¹⁰ Lewis JA (2019), In-Water Hull Cleaning Trial: Sydney, February 2019: Water Quality Monitoring of Discharges. Report prepared for CleanSubSea, Henderson, WA. ES Link Services Pty Ltd.

Surroundings

	μg Cu /L		
	Total conc.	Freely dissolved	
Maximum conc.	0.0023	0.0015	
95% conc.	0.0014	0.0009	
Average conc.	0.0005	0.0003	
Minimum conc.	<0.0001	<0.0001	

Trigger values for copper at alternative levels of protection³

Trigger values for marine water (μg Cu/L)			
Species Protection Level			
80%	90%	95%	99%
8	3	1.3	0.3

Comparison of the PECs from MAMPEC with the ANZECC/ARMCANZ trigger values shows that copper discharge from one day of cleaning would result in an environmental concentration an order of magnitude below the 99% Species Protection Level, and two orders of magnitude below the 90% Species Protection Level. Using the Morrisey et al. criteria of low risk defined as average PEC below the ANZECC 90% protection guideline, the discharge from a cleaning operation is classified as low risk.

Calculation of RQ from the PECs also results in a low risk determination (i.e. < 1.0):

PEC/PNEC = 0.02/2.6

RQ = 0.0077

Critical Discharge Concentrations

The critical concentrations of copper in the discharge can be back calculated using the MAMPEC model. For the RQ method, a PEC of 2.6 μ g Cu/L would result in an RQ of unity and, applying Species Protection Level trigger values, the PEC should be no more than 3 μ g Cu/L (90% protection). Running the model for 10-fold increases in the discharge concentration based on trial measurements gives the following results:

Discharge Concentration	PEC (u	g Cu/L)
(mg Cu/L)	Average	Мах
0.05	0.0214	0.0398
0.50	0.214	0.398
5.00	2.14	3.98

Using these results as a guide, and trial and error, running the model for different discharge concentrations enabled the concentrations that would result in critical PECs to be determined as follows:

Critical PEC	Discharge Conc.
(ug Cu/L)	(mg Cu/L)
8 [SPL 80%]	18.75
3 [SPL 90%]	7.05
2.6 [PNEC]	6.10
1.3 [SPL 95%]	3.05
0.3 [SPL 99%]	0.70

These values further demonstrate that the concentrations measured in the effluent at discharge during cleaning operations are well below those that could result in an environmental concentration of concern.

Conclusions and Recommendations

- The MAMPEC-BW model can be used to predict environmental contaminant concentrations for antifouling biocides discharged in the effluent from in-water hull cleaning waste treatment systems during cleaning operations.
- From daily discharge volumes and contaminant concentrations measured during *Envirocart* trials, and using Lyttelton Harbour as the example port, the resultant PECs for copper were an order of magnitude below that needed to meet the highest protection level in the Australian and New Zealand Guidelines for Fresh and Marine Water Quality
- A shut down trigger value for contaminant concentration has been suggested for use during cleaning
 operations to ensure that treatment processes are effectively removing contaminants from the waste
 stream. From the MAMPEC modelling, a trigger concentration of 0.5 mg Cu/L is suggested as providing
 a suitable and conservative protection level.

Glossary

Term	Definition
Hull grooming	Cleaning of hull surfaces (not niches) to remove primary biofouling and early stages of secondary biofouling to improve ship performance
IWC	In-water cleaning
Primary biofouling	Also known as 'slime', the layer of microscopic organisms that may include bacteria, diatoms and/or protozoans and the extracellular products they produce, and the microscopic, early settlement stages of secondary biofouling organisms
Proactive IWC	Cleaning of hull surfaces and/or niches to remove early stages of biofouling and prevent the growth and maturation of macrofouling organisms
Reactive IWC	Cleaning of hull surfaces and/or niches to remove established secondary biofouling and associated tertiary biofouling organisms if present
Secondary biofouling	Macroscopic sessile organisms, visible to the naked eye, that are attached directly to the substrate.
Tertiary stage biofouling	Secondary biofouling with additional macroscopic sessile or mobile organisms growing on or in interstices between the secondary biofouling organisms

References

ABS 2007, Guidance notes on the inspection and application of marine coating systems, Third edition, American Bureau of Shipping, Houston, TX.

Akzo Nobel 2016, Organotins in Intersleek 29th July 2016, Akzo Nobel, Felling, UK.

Almeida, E, Diamantino, TC & de Sousa, O 2007, Marine paints: the particular case of antifouling paints', Progress in Organic Coatings, 59, 2-20.

Al-Saydeh, SA, El-Naas, MH & Zaidi, SJ 2017, 'Copper removal from industrial wastewater: A comprehensive review', Journal of Industrial and Engineering Chemistry, 56, 35-44.

Amara, I, Miled, W, Ben Slama, R & Ladhari, N 2018, 'Antifouling processes and toxicity effects of antifouling paints on marine environment: A review', Environmental Toxicology and Pharmacology, 57, 115-130.

ANZECC/ARMCANZ 2000, Australian and New Zealand Guidelines for Fresh and Marine Water Quality, Australian and New Zealand Environment and Conservation Council & Agriculture and Resource Management Council of Australia and New Zealand.

APVMA 2005, Notice: copper pyrithione, Commonwealth of Australia Gazette no. APVMA 2, 1 February 2005, 12.

APVMA 2015a, Diuron Chemical Review, Australian Government, Australian Pesticides and Veterinary Medicines Authority, accessed 21 March 2020.

APVMA 2015b, Dithiocarbamates – priority 1, Australian Government, Australian Pesticides and Veterinary Medicines Authority, accessed 21 March 2020.

APVMA 2020a, Anti-fouling paint for use on boat hulls: guidance document, March 2020, Australian Government, Australian Pesticides and Veterinary Medicines Authority, Sydney, NSW.

APVMA 2020b, Anti-fouling paint for use on boat hulls: Environmental assessment, March 2020, Australian Government, Australian Pesticides and Veterinary Medicines Authority, Sydney, NSW.

APVMA 2020c, Public Chemical Registration Information System Search, Australian Pesticides and Veterinary Medicines Authority.

APVMA 2020d, Agriculture data guidelines; Environment (Part 7), Australian Pesticides and Veterinary Medicines Authority.

Atlar, M, Glover, E, Candries, M, Mutton, R & Anderson, C 2002, The effect of a foul release coating on propeller performance, in Marine Science and Technology for Environmental Sustainability, Proceedings, University of Newcastle upon Tyne, Newcastle upon Tyne, UK.

Ayers, JC & Turner, HJ 1952, 'The principal fouling organisms', pp. 118-164 in, Woods Hole Oceanographic Institution, Marine fouling and its prevention, United States Naval Institute, Annapolis, MA.

Batra, SN 2014. 'A guide to hull painting of ships', Marine Insight, Bangalore, India.

Blossom, N, Anderson, C, Lewis, J & Stuchik, A 2016, 'Copper in antifoulings: going from strength to strength', Paint & Coatings Industry Magazine, August 2016, 34-38.

Blunden, SJ & Chapman, A 1986, 'Organotin compounds in the environment', pp. 111-159 in, Craig, PJ, Organometallic compounds in the environment: principles and reactions, Wiley, New York.

Bohlander, J 2009, Review of options for in-water cleaning of ships, MAF Biosecurity New Zealand Paper No: 2009/42, MAF Biosecurity New Zealand, Wellington, NZ.

Bohnes, H & Franke, G 1997, 'Galavanic (sacrificial) anodes', pp. 179-206 in, Prinz, W, von Baeckmann, W & Schwenk, W, Handbook of corrosion protection, Gulf Publishing Company, Houston, TX.

Bressy, C, Margaillan, A, Faÿ, F, Linnossier, I & Réhel, K 2009, 'Tin-free self-polishing marine antifouling coatings', pp. 445-491 in, Hellio, C & Yebra, D, Advances in marine antifouling coatings and technologies, Woodhead Publishing Limited, Cambridge, UK.

Brooks, S & Waldock, M, 2009a, 'Copper biocides in the marine environment', pp. 413-428 in, Arai, T, Harino, H, Ohji, M & Langston, WH, Ecotoxicology of antifouling biocides, Springer, Tokyo, Berlin, Heidelberg, New York.

Brooks, S & Waldock, M, 2009b, 'The use of copper as a biocide in marine antifouling paints', pp. 492-521 in, Hellio, C & Yebra, D, Advances in marine antifouling coatings and technologies, Woodhead Publishing Limited, Cambridge, UK.

California Water Boards 2013, In-water vessel hull cleaning: Best management practice, Fact Sheet – July 2013, State Water Resources Control Board, Sacramento, CA.

Cassé, F & Swain GW 2006, 'The development of microfouling on four commercial antifouling coatings under static and dynamic conditions', International Biodeterioration & Biodegradation, 57, 179-185.

Callow, ME 1990, 'Ship fouling: problems and solutions', Chemistry & Industry, 5 March 1990, 123-127.

Callow, ME 1996, 'Ship fouling: the problem and methods of control', Biodeterioration Abstracts, 10, 411-421.

Carlton, JS 2019, Marine propellers and propulsion, 4th Edition, Butterworth-Heinemann, Oxford, UK.

Chasse, KR, Scardino, AJ & Swain, GW 2020, 'Corrosion and fouling study of copper-based antifouling on 5083 aluminium alloy', Progress in Organic Coatings, 141, 105555.

Chouyyok, W, Shin, Y, Davidson, J, Samuels, WDE, Lafemina, NH, Rutledge, RD & Fryxell, GE, 2010, 'Selective removal of copper(II) from natural waters by nanoporous sorbents functionalized with chelating diamines', Environmental Science & Technology, 44, 6390-6395.

CoA 2009, National assessment guidelines for dredging, Commonwealth of Australia, Canberra, ACT.

Coutts, ADM & Dodgshun, TJ 2007, 'The nature and extent of organisms in vessel sea-chests: a protected mechanism for marine invasions', Marine Pollution Bulletin 54, 875-886.

Crawl, F 2014, 'Selektope in antifouling fast lane', International Bulk Journal, 5, 51-52.

Dafforn, KA, Lewis, JA & Johnston, EL, 2011, 'Antifouling strategies: history and regulation, ecological impacts and mitigation', Marine Pollution Bulletin, 62, 453-465.

Davidson, I, Scianni, C, Hewitt, C, Everett, R, Holm, E, Tamburri, M & Ruiz, G 2016, 'Mini-review: Assessing the drivers of ship biofouling management – aligning industry and biosecurity goals', Biofouling, 32, 411-428.

Davies, AG 2010, 'Organotin compounds in technology and industry', Journal of Chemical Research, 34, 181-190.

DNV-GL 2020, IMO Sub-Committee on Pollution Prevention and Response, Technical Regulatory News No.04/2020 – Statutory, DNV GL, Hamburg, Germany.

DoA/NZMPI 2015, Department of the Environment and New Zealand Ministry for Primary Industries, Anti-fouling and in-water cleaning guidelines, April 2015, Department of Agriculture, Canberra, ACT.

Doi, H 1982, 'Takata 'Sea Queen' anti-slime A/F developed', Zosen, 26 (13), 34-40.

Dürr, S 2010, 'Preface', pp. xv-xix in, Dürr, S & Thomason, JC, Biofouling, Wiley-Blackwell, Chichester, UK.

Ecology WA 2019, Antifouling paints in Washington State: Report and recommendations, Report the legislature pursuant to SHB 2634 (2018), Publication 19-04-020, Department of Ecology, State of Washington, USA.

Edyvean, RGJ & Silk, NJ 1988, 'The sulphide induced discoloration of copper containing antifouling paints', Biofouling, 1, 269-277.

EPA 2013a, Application for the reassessment of a group of hazardous substances: APP201051 – Antifouling paints, Environmental Protection Authority, New Zealand Government, January 2013.

EPA 2013b, Evaluation and review report: APP201051 – Antifouling paints, Environmental Protection Authority, New Zealand Government, May 2013.

EPA 2013c, Decision: Application for the reassessment of a group of hazardous substances: APP201051 – Antifouling paints, Environmental Protection Authority, New Zealand Government, June 2013.

EPA 2020, Is your boat paint legal to import and manufacture? Environmental Protection Authority, New Zealand Government, accessed 21 March 2020.

Fent, K & Hunn, J 1995, 'Organotins in freshwater harbors and rivers: temporal distribution, annual trends and fate', Environmental Toxicology and Chemistry, 14, 1123-1132.

Ferry, JD & Ketchum, BH 1952, 'Mechanism of release of toxics from paints", pp. 277-301 in, Woods Hole Oceanographic Institution, Marine fouling and its prevention, United States Naval Institute, Annapolis, MA.

Finnie, AA 2006, 'Improved estimates of environmental copper release rates from antifouling products', Biofouling, 22, 279-291.

Finnie, AA & Williams DN 2010, 'Paints and coatings technology for the control of marine fouling', pp. 185-206 in, Dürr, S & Thomason, JC, 'Biofouling', Wiley-Blackwell, Chichester, UK.

Fitzsimons, B 2011, Fitz's Atlas 2 of coating defect, MPI Group, Farnham, UK.

Fletcher, LE & Lewis, J 1999, 'Regulation of shipyard discharges in Australia and the potential of UV oxidation for TBT degradation in washdown water', pp. 27-36 in, Champ, MA, Fox, TJ & Mearns, AJ, Proceedings of the Special Sessions held at Oceans '99 in Seattle, Washington, Sept 13-16, 1999 on: Treatment of Regulated Discharges from Shipyards and Drydocks, Volume No. 4, The Marine Technology Society, Washington, DC.

Floerl, O, Inglis, GJ & Hayden, BJ 2005, 'A risk-based predictive tool to prevent accidental introductions of nonindigenous marine species', Environmental Management, 35, 765-778.

Francis, R 2012, 'Galvanic corrosion', pp. 74-89 in, Powell, C & Francis, R, The corrosion performance of metals for the marine environment: as basic guide, Maney Publishing, Leeds, UK.

Frey, MA, Simard, N, Robichaud, DD, Martin, JL & Therriault, TW 2014, 'Fouling around: vessel sea-chests as a vector for the introduction and spread of aquatic invasive species', Management of Biological Invasions, 5, 21-30.

Gadd, J, Depree, C & Hickey, C 2011, Relevance to New Zealand of the OECD Emission Scenario Document for Antifouling Products: Phase 2 Report, NIWA Client Report HAM 2011-005, National Institute of Water & Atmospheric Research Ltd, Hamilton, NZ.

Georgiades, E, Growcott, A & Kluza, D 2018. Technical guidance on biofouling management for vessels arriving to New Zealand, MPI Technical Paper No; 2018/07, Ministry for Primary Industries, Wellington, NZ.

Goldie, B 2015, 'Nontoxic barnacle antifouling', Journal of Protective Coatings & Linings, 32, 65-70.

Hearin, J, Hunsucker, KZ, Swain, G, Stephens, A, Gardner, H, Lieberman, K & Harper, M 2015, 'Analysis of long term mechanical grooming on large-scale test panels coated with an antifouling and a fouling release coating', Biofouling, 31, 625-638.

Hearin, J, Hunsucker, KZ, Swain, G, Gardner, H, Stephens, A & Lieberman, K 2016, 'Analysis of mechanical grooming at various frequencies on a large scale test panel coated with a fouling-release coating', Biofouling, 32, 561-569.

HSE 2004, Operational Circular OC 730/15: marine anti-fouling coatings, Health and Safety Executive, UK.

HSE 2020, UK Active Substance Database, Health and Safety Executive, UK.

Hunsucker, KZ, Vora, GJ, Hunsucker, JT, Gardner, H, Leary, DH, Kim, S, Lin, B & Swain, G 2018, 'Biofilm community structure and the associated drag penalties of a groomed fouling release ship hull coating', Biofouling, 34, 162-172.

Hydrex 2012, Ship propeller maintenance: polish or clean? Hydrex nv, Antwerp, Belgium.

IMO 2005, Anti-fouling systems: International Convention on the Control of Harmful Anti-Fouling Systems on Ships, 2005 Edition, International Maritime Organization, London, UK.

IMO 2020, Status of Treaties (18/05/2020), International Maritime Organization.

IPPIC 2012, Function of zinc oxide in antifouling paints, International Paint & Printing Ink Council, Washington DC, USA.

ISO 2010, Paints and varnishes – modelling of biocide release rate from antifouling paints by mass-balance calculation, International Standard ISO 10890:2010, International Organization for Standardization, Geneva, Switzerland.

I-Tech 2020, Selektope®, I-Tech AB, Mölndal, Sweden.

Jackson, SM & Jones, EBG 1988, 'Fouling film development on antifouling paints with special reference to film thickness', International Biodeterioration, 24, 277-287.

Janssen 2016, Econea[®], Marine Antifouling Agent, Janssen Pharmaceutica, Beerse, Belgium.

Jotun 2020, Jotun Hull Skating Solutions: Join the REVHULLUTION, Jotun A/S, Sanderfjord, Norway.

Khulbe, KC & Matsuura, T 2018, 'Removal of heavy metals and pollutants by membrane adsorption techniques', Applied Water Science, 8, 19.

Konstantinou, IK & Albanis, TA 2004, 'Worldwide occurrence and effects of antifouling paint booster biocides in the aquatic environment: a review', Environment International, 30, 235-248.

Korkut, E & Atlar, M 2012, 'An experimental investigation of the effect of foul release coating application on performance, noise and cavitation characteristics of marine propellers', Ocean Engineering, 41, 1-12Lee, RF 1996, 'Metabolism of tributyltin by aquatic organisms', pp. 369-382 in, Champ MA & Seligman PF, 'Organotin', Chapman & Hall, London.

Lejars, M, Maragaillan, A & Bressy, C 2012, 'Fouling release coatings; a nontoxic alternative to biocidal antifouling coatings', Chemical Reviews, 112, 4347-4390.

Lewis, JA 1998, 'Marine biofouling an its prevention on underwater surfaces', Materials Forum, 22, 41-61.

Lewis, JA 2002, Hull fouling as a vector for the translocation of marine organisms: Report 2 – The significance of the prospective ban on tributyltin antifouling paints on the introduction and translocation of marine pests in Australia, Ballast Water Research Series, Report no. 15, Department of Agriculture, Fisheries and Forestry, Canberra, ACT. Lewis, JA 2009, 'Non-silicone biocide-free antifouling solutions', pp. 709-724 in, Hellio C & Yebra D, Advances in marine antifouling coatings and technologies, Woodhead Publishing Limited, Cambridge, UK.

Lewis, JA 2010, Review of the ANZECC Code: antifouling coatings technical summary, Report to Ministry of Agriculture and Forestry, New Zealand, by ES Link Services Pty Ltd, Castlemaine, Vic.

Lewis, JA 2013, In-water hull cleaning and filtration system: in-water cleaning trials, 26-28 November 2012, Fisheries Occasional Publication No. 114, Department of Fisheries, Perth, WA.

Lewis, JA 2016, Project 16214, Assessment of preventative biofouling management measures, MPI Technical Paper No: 2016/69, Ministry for Primary Industries, Wellington, NZ.

Lewis, JA 2018, 'Battling biofouling with, and without, biocides', Chemistry in Australia, June 2018, 26-29.

Lindner, E 1988, 'Failure mechanism of copper antifouling coatings', International Biodeterioration, 24, 247-253.

Luoma, SN & Rainbow, PS 2008, Metal contamination in aquatic environments: science and lateral management, Cambridge University Press, New York

MME 2020, Sacrificial anodes, MME Group, Ridderkerk, The Netherlands.

Molino, PJ & Wetherbee, R 2008, 'The biology of biofouling diatoms and their role in the development of microbial slimes", Biofouling, 24, 365-379.

Morgan, JH 1987, Cathodic protection, 2nd edition, NACE International, Houston, TX.

Morrisey, D, Gadd, J, Page, M, Floerl, O, Woods, C, Lewis, J, Bell, A & Georgiades, E 2013, In-water cleaning of vessels: biosecurity and chemical contamination risks, MPI Technical Paper No: 2013/11, Ministry for Primary Industries, Wellington, NZ.

Morrisey, D & Woods, C 2015, In-water cleaning technologies: review of information, MPI Technical Paper No: 2015/38, Ministry for Primary Industries, Wellington, NZ.

NRA 2001, Public release summary on evaluation of the new active zinc pyrithione in the product International Intersmooth 360 Ecoloflex Antifouling, National Registration Authority for Agricultural and Veterinary Chemicals, Canberra.

NSSC 2006, Naval Ship's Technical Manual, Chapter 081, Waterborne underwater hull cleaning of navy ships, Naval Sea Systems Command, United States Navy.

Oliveira, DR & Granhag, L 2020, 'Ship hull in-water cleaning and its effects on fouling-control coatings', Biofouling, 3e6, 332-350.

Omae, I 2006, 'Chemistry and fate of organotin antifouling biocides in the environment', pp. 17-50 in, Konstantinou, I, The Handbook of Environmental Chemistry 5.0, Antifouling paint biocides, Springer Verlag, Berlin Heidelberg.

OSHA 2014, <u>Dibutyltin Dilaurate as Sn</u>, Occupational Safety & Health Administration, United States Department of Labor, Washington, DC.

Powell, C 2012, 'Introduction', pp. 1-2 in, Powell, C & Francis, R, The corrosion performance of metals for the marine environment: as basic guide, Maney Publishing, Leeds, UK.

Powell, C & Webster, P 2012, 'Copper alloys', pp. 26-41 in, Powell, C & Francis, R, The corrosion performance of metals for the marine environment: as basic guide, Maney Publishing, Leeds, UK.

RD Instruments 2002, Using acoustic windows, Application Note FSA-010 (December 2002), RD Instruments.

Redfield, AC 1952, 'The fouling of metallic surfaces", pp. 349-364 in, Woods Hole Oceanographic Institution, Marine fouling and its prevention, United States Naval Institute, Annapolis, MA.

Rolands, JC & Angell, B 1976, Corrosion for marine and offshore engineers, IMarEST, London.

Scarlett, A, Donkin, P, Fileman, TW, Evans, SV & Donkin, ME 1999a, 'Risk posed by the antifouling agent Irgarol 1051 to the seagrass, *Zostera marina*', Aquatic Toxicology, 45, 159-170.

Scarlett, A, Donkin, P, Fileman, TW & Morris, RJ 1999b, 'Occurrence of the antifouling herbicide, Irgarol 1051, within coastal-water seagrasses from Queensland', Marine Pollution Bulletin, 38, 687-691.

Sea Hawk 2020, Product information: Islands 44 Plus™ HARDER, Sea Hawk, Clearwater, USA

Selektope 2020, Commercial marine coatings that contain Selektope, I-Tech AB, Mölndal, Sweden.

Seligman, PF, Maguire, RJ, Lee, RF, Hinga, KR, Valkirs, AO & Stang, PM 1996, 'Persistence and fate of tributyltin in aquatic systems', pp. 429-457in, Champ MA & Seligman PF, Organotin, Chapman & Hall, London.

Shilton, C 1997, 'Mechanism of action of tin-free antifouling paints: Intersmooth 360 Ecoloflex', Pitture e Vernici, 73, 10-18.

Sinclair, MD 2003, 'A review of the physiological effects of α_2 -agonists related to the clinical use of medetomidine in small animal practice', The Canadian Veterinary Journal, 44, 885-897.

Soroldoni, S, da Silva, SV, Castro, IB, Martins, CMG & Pinho, GLL 2020, 'Antifouling paint particles cause toxicity to benthic organisms: effects on two species with different feeding modes', Chemosphere, 238, 124610.

Standards Australia 2016, Australian Standard AS 2239-2003 (R2016), Galvanic (sacrificial) anodes for cathodic protection, Standards Australia International Ltd, Sydney.

Subsea World News 2019, HullWiper set to launch hull cleaning services in Qatar, www.offshore-energy.biz.

Swain, G 2019, 'In-water grooming to maintain ship hulls: from research to reality', Presentation 12-1, 4th ANZPAC Workshop on Biofouling Management for Sustainable Shipping / 1st GEF-UNDP-IMO GloFouling R&D Forum and Exhibition on Biofouling Management, Melbourne, Vic, October 2019.
Takahashi, CK, Turner, A, Millwards, GE & Glegg, GA 2012, 'Persistence and metallic composition of paint particles in sediments from a tidal inlet', Marine Pollution Bulletin, 64, 133-137.

Tamburri, MN, Davidson, IC, First, MR, Scianni, C, Newcomer, K, Inglis, GJ, Georgiades, ET, Barnes, JM & Ruiz, GM 2020, 'In-water cleaning and capture to remove ship biofouling: an initial evaluation of efficacy and environmental safety', Frontiers in Marine Science, 7, 437.

Taylor, GE & Evans, LV 1976, 'The biology of slime films, Part 1', Shipping World & Shipbuilder, October 1976, 857-858.

TCS 2004, Antifouling performance standards for the maritime industry: Development of a framework for the assessment, approval and relevance of effective products, A consultancy for the Natural Heritage Trust, Thompson Clarke Shipping Pty. Ltd. in association with CTI Consultants Pty. Ltd. and Mr John A. Lewis.

The Iron and Steel Institute 1944, Fouling of ships' bottoms: identification of marine growths, The Iron and Steel Institute, London, UK.

The Maritime Executive 2020, ECOsubsea gains further foothold in major European ports, www.maritime-executive.com.

Thomas, K 2009, 'The use of broad-spectrum organic biocides in marine antifouling paints', pp. 522-553 in, Hellio C & Yebra D, Advances in marine antifouling coatings and technologies, Woodhead Publishing Limited, Cambridge, UK.

Thomas, KV & Brooks, S 2010, 'The environmental fate and effects of antifouling paint biocides', Biofouling, 26, 73-88.

Thomas, TE & Robinson, MG 1986, 'The physiological effects of the leachates from a selfpolishing organotin antifouling paint on marine diatoms', Marine Environmental Research, 18, 215-229.

Thomason, JC 2010, 'Fouling on shipping: data-mining the world's largest antifouling archive', pp. 207-216 in, Dürr, S & Thomason, JC, 'Biofouling', Wiley-Blackwell, Chichester, UK.

Tribou, M & Swain, G 2010, 'The use of proactive in-water grooming to improve the performance of ship hull antifouling coatings', Biofouling, 26, 47-56.

Tribou, M & Swain, G 2017, 'The effects of grooming on a copper ablative coating: a six-year study', Biofouling, 33, 494-504.

Turner, A 2010, 'Marine pollution from antifouling paint particles', Marine Pollution Bulletin, 60, 159-171.

US EPA 1995, Ambient water quality criteria-saltwater copper addendum (Draft), April 14, Office of Water, Office of Science and Technology, United States Environmental Protection Agency, Washington, DC.

US EPA 2007, Notice of Pesticide Registration, EPA Reg. Number: 43813-27, Econea Technical, United States Environmental Protection Agency, Office of Pesticides Programs, Washington, DC.

US EPA 2019, Label Amendment, Pettit Hydrocoat ECO Copper Free Multi-Season Ablative, EPA Registration Number: 60061-137, United States Environmental Protection Agency, Office of Chemical Safety and Pollution Prevention, Washington, DC.

van Hattum, B, van Gils, J, Markus, A, Jansen, M & Baart, A 2016, MAMPEC 3.1 Handbook, Technical documentation, Deltares, Delft, The Netherlands.

van Hattum, B, van Gils, J, Markus, A, Elzinga, H, Kleisse, F & Baart, A 2018, User manual – quick guide, MAMPEC 3.1, MAMPEC-BW 3.1, Deltares, Delft, The Netherlands.

Vardhan, DH, Ramesh, A & Reddy, BCM 2019, 'A review on materials used for marine propellers', Materials Today: Proceedings, 18, 4482-4490.

Widdows, J & Page, DS 1993, 'Effects of tributyltin and dibutyltin on the physiological energetics of the mussel *Mytilus edulis*', Marine Environmental Research, 35, 233-249.

Wisely, B 1958, 'The settling and some experimental reactions of a bryozoan larva, *Watersipora cucullata* (Busk)', Australian Journal of Marine and Freshwater Research, 9, 362-371.

Wood, EJF & Allen, FE 1958, Common marine fouling organisms of Australian waters, Navy Office, Melbourne.

Woods, DC, Fletcher, RL & Jones, EBG 1988, 'Microfouling film composition, thickness, and roughness on ship trial antifouling paints', pp. 49-56 in, Houghton, DR, Smith, RN & Eggins, HOW, Biodeterioration 7, Elsevier Applied Science, London & New York.

Yebra, DM, Kiil, S & Dam-Johansen, K 2004, 'Antifouling technology – past, present and future steps towards efficient and environmentally friendly antifouling coatings, Progress in Organic Coatings, 50, 75-104.

Yebra, DM, Kiil, S, Weinell, CE & Dam-Johansen, K 2006, 'Presence and effects of marine microfilms on biocide-based antifouling paints', Biofouling, 22, 33-41.

Zainzinger, V 2019, 'Antifouling coatings cling to copper', Chemistry World, 21 January 2019.